



DOCUMENT NAME] SPECIFICATION  
[TITLE OF THE INVENTION]  
IMAGE FORMING METHOD USING PHOTOTHERMOGRAPHIC MATERIAL

[WHAT IS CLAIMED IS]

[Claim 1] An image forming method using a photothermographic material comprising, on a surface of a support, a photosensitive silver halide, a non-photosensitive organic silver salt, a thermal developer and a binder, wherein the photothermographic material has a gamma value of 2.0 to 4.0 at an optical density of 1.2 in a photographic characteristic curve and is thermally developed while conveyed at a speed of not less than 23 mm/sec.

[Claim 2] An image forming method using a photothermographic material comprising, on a surface of a support, a photosensitive silver halide, a non-photosensitive organic silver salt, a thermal developer and a binder, wherein the photothermographic material has a gamma value of 2.0 to 4.0 at an optical density of 1.2 in a photographic characteristic curve and is developed in a thermal developing device configured such that a distance between an exposing section and a developing section is 0 cm to 50 cm.

[Claim 3] The method of claim 1 or 2, wherein the photosensitive silver halide includes at least two types of silver halide emulsions having different grain sizes.

[Claim 4] The method of any one of claims 1 to 3, wherein the photosensitive silver halide is added during preparation of the non-photosensitive organic silver salt.

[Claim 5] The method of any one of claims 1 to 4, wherein two or more photosensitive emulsion layers containing the photosensitive silver halide are provided.

[Claim 6] The method of any one of claims 1 to 5, wherein the photothermographic material is a sheet-like material and the photothermographic material begins to be developed at an exposed portion thereof while another portion is still being exposed.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical Field of the Invention]

The present invention relates to a method of forming an image using a light-sensitive thermal developing material (hereinafter occasionally referred to as the "photothermographic material"). More particularly, the present invention relates to a method of forming an image using a photothermographic material that provides stable output images with little difference in color tone even in a thermal developing apparatus with high line speed at the time of thermal development.

[0002]

[Prior Art]

Recently, in the field of films for medical imaging and the field of films for graphic arts, there is a strong demand for reduction in the volume of waste processing liquid from the viewpoint of environmental preservation and economy of space. There have been demands for technologies relating to use of a photothermographic material as a film for medical imaging and a film for graphic arts. In particular, there is a demand for a photothermographic material that is efficiently exposed by a laser image setter or a laser imager, and provides black-toned images with high resolution and sharpness. Such a

photothermographic material can provide users with a simpler and ecological thermal developing system without the use of liquid processing chemicals.

[0003]

Although there are similar demands in the field of general image forming materials, high image quality (i.e., excellent sharpness and fine graininess) is particularly required for images used in medical imaging where high image quality of excellent sharpness and granularity is necessary. Further, images with blue-black tones are preferred from the perspective of facilitating diagnosis. Various types of hard copy systems using pigment or dye, such as an inkjet printer and an electrophotographic system, are commonly used as a general image forming system. But none of these is satisfactory as an output system for medical images.

[0004]

In general, thermal image forming systems using organic silver salts are described in, for example, a non-patent document 1.

A photothermographic material typically includes a photosensitive layer in which a catalytically active amount of a photocatalyst (e.g., silver halide), a reducing agent, reducible silver salt (e.g., organic silver salt) and a toner for controlling the tone of a developed silver image as needed are dispersed in the matrix of a binder.

After an image is exposed thereon, a photothermographic material is heated to a high temperature (e.g., 80 °C or above) to cause an oxidation-reduction reaction between reducible silver salt (which acts as an oxidizing agent) and a reducing agent, thus providing a black silver image. The oxidation-reduction reaction is accelerated by the catalytic action of a latent image of the exposed silver halide (see patent documents 1 and 2).

[0005]

There has always been a demand for improving processing capacity of the thermal developing process and thereby reducing processing time for the above-described photothermographic materials. In order to respond to such a demand, the conveyance speed (line speed) during the development needs to be increased. Particularly, when a portion of a sheet of photosensitive material is exposed while another portion of the sheet which has already been exposed is developed, the photosensitive material may be vibrated by rollers or the like when the rollers hold the photosensitive material for conveyance, whereby blurred images are formed. This subtle blurring in development has been a serious problem because it causes difference in color tone on the sheet of photosensitive material and stability of output images deteriorates.

This problem is feared to be taken more seriously as reduction in the processing time is in progress.

[0006]

Thus, it is very difficult to achieve a rapid developing process and image stability at the same time by removing blurring in development.

[0007]

[Patent Document 1]

United States Patent (USP) No. 2910377

[Patent Document 2]

Japanese Patent Application Publication (JP-B) No. 43-4924

[Non-Patent Document 1]

"Thermally Processed Silver Systems," (Imaging Processes and Materials) Neblette, 8th edition, edited by D. Klosterboer, compiled by J. Sturge, V. Walworth and A. Shepp, Chapter 9, page 279, 1989

[0008]

[Problems to be Solved by the Invention]

The present invention intends to solve the above problems in the prior art and has an object to provide a method of forming an image using a photothermographic material that provides stable output images with little difference in color tone even in a thermal developing apparatus with high line speed at the time of thermal development.

[0009]

[Means for Solving the Problems]

The object of the present invention is achieved by the following photothermographic material:

(1) An image forming method using a photothermographic material comprising, on a surface of a support, a photosensitive silver halide, a non-photosensitive organic silver salt, a thermal developer and a binder, wherein the photothermographic material has a gamma value of 2.0 to 4.0 at an optical density of 1.2 in a photographic characteristic curve and is thermally developed while conveyed at a speed of not less than 23 mm/sec.

(2) An image forming method using a photothermographic material comprising, on a surface of a support, a photosensitive silver halide, a non-photosensitive organic silver salt, a thermal developer and a binder, wherein the photothermographic material has a gamma value of 2.0 to 4.0 at an optical density of 1.2 in a photographic characteristic curve and is developed in a thermal developing device configured such that a distance between an exposing section and a developing section is 0 cm to 50 cm.

(3) The method of (1) or (2), wherein the photosensitive silver halide includes at least two types of silver halide emulsions having different grain sizes.

(4) The method of any one of (1) to (3), wherein the photosensitive silver halide is added during preparation of the non-photosensitive organic silver salt.

(5) The method of any one of (1) to (4), wherein two or more photosensitive emulsion layers containing the photosensitive silver halide are provided.

(6) The method of any one of (1) to (5), wherein the photothermographic material is a sheet-like material and the photothermographic material begins to be developed at an exposed portion thereof while another portion is still being exposed.

[0010]

The present invention will be described below in detail.

[0011]

[Embodiments]

#### 1. Photographic characteristic curve

In the present invention, a photographic characteristic curve is a D-log E curve representing a relationship between the common logarithm (log E) of a light exposure, i.e., the exposure energy, and the optical density (D), i.e., a scattered light photographic density, by plotting the former on the abscissa and the latter on the ordinate. A gamma ( $\gamma$ ) value represents a tangent angle when the optical density D on the photographic characteristic curve is 1.2 (i.e.,  $\gamma$  value equals  $\tan \theta$  when the angle between the tangent and the abscissa is  $\theta$ ).

[0012]

It is well known that a maximum optical density and a gamma ( $\gamma$ ) value in the photographic characteristic curve have some effects on image quality such as sharpness and contrast of an image. To obtain a satisfactory image quality for photothermographic materials used in a laser image setter or a laser imager (i.e., LI photosensitive materials), the maximum optical density and the gamma ( $\gamma$ ) value have been adjusted. In such a conventional technique, however, problems such as occurrence of subtle blurring in development caused by reduced processing time have not been recognized. Moreover, no countermeasures have been taken for decreased stability in output images or such problems have not been approached in view of selecting ideal photothermographic materials.

[0013]

The present inventors have found that conveyance of photosensitive materials at high-speed or contact of the photosensitive materials with a conveyance roller causes vibration on the sensitive materials, thereby causing output images to become unstable. The present inventors have also found that the image quality of the output images is improved remarkably when a photothermographic material having a gamma value of 2.0 to 4.0 at an optical density of 1.2 in the photographic characteristic curve is used. Such a photothermographic material can form images stably even under such vibration. The gamma value is preferably 2.5 to 3.5, and more preferably 2.0 to 3.0. If the gamma value at optical density of 1.2 is smaller than 2.0, image density becomes insufficient to obtain satisfactory image quality. If the gamma value is larger than 4.0, blurring in thermal development due to high-speed conveyance occurs easily.

[0014]

The characteristic curve in the present invention can be shifted by various methods, such as by changing the amount of silver halide to be added, by changing the average grain size, by employing another method for chemical sensitization, by changing the degrees of ripening, or by changing the type or the amount of a spectral sensitizing dye adsorbing to the silver halides.

When a silver halide emulsion is used singly, the gamma value can be changed by, for example, (1) changing the grain size distribution of the silver halide, (2) employing another method of chemical sensitization, (3) controlling the heavy metal added to the silver halide, (4) changing the type or the amount of spectral sensitizing dye adsorbing to the silver halides or (5) changing halogen composition of the silver halide.

When at least two silver halide emulsions having different photosensitivity are used, the gamma value can be changed by, for example, (1) employing silver halides having different grain sizes, (2) employing silver halides which have been chemically sensitized in different ways, (3) employing silver halides with different heavy metals added thereto, (4) employing silver halides with different types or amounts of spectral sensitizing dye adsorbing to the silver halides or (5) employing silver halides with different halogen compositions of the silver halide.

The gamma value can also be changed by adding at least two types of silver halides having different photosensitivity to at least two different image forming layers.

[0015]

The grain size distribution of the silver halide can be changed by, for example, employing at least two types of silver halides having different grain sizes mixed together, or employing silver halide having a wide range of grain size distribution. It is also preferable to apply at least two types of silver halides having different grain sizes onto different two image forming layers.

The silver halide can be sensitized by, for example, employing a chemically sensitized silver halide, or changing the type of chemical sensitizing agent or the degree of sensitization. It is also preferable to employ at least two types of silver halides with different types of chemical sensitizing agent or sensitized to different degrees, that are mixed together or applied onto two different image forming layers.

The heavy metal added to the silver halide can be controlled by, for example, changing the types or the amounts of the heavy metal, or employing at least two types of silver halides with different types of heavy metals mixed together or applied onto two different image forming layers.

It is also preferable to mix at least two types of silver halides with different types or amounts of spectral sensitizing dyes or to apply the silver halides onto two different image forming layers.

It is also preferable to mix at least two types of silver halides with different halogen compositions or to apply the silver halides onto two different image forming layers.

[0016]

Now, a composition of the photothermographic material will be described in detail, along with the effects of these compounds on the characteristic curve.

[0017]

## 2. Photosensitive silver halide

### 1) Halogen composition

For the photosensitive silver halide used in the invention, there is no particular restriction on the halogen composition, and silver chloride, silver bromochloride, silver bromide, silver bromoiodide, silver chlorobromoiodide and silver iodide can be used. Among them, silver bromide, silver bromoiodide and silver iodide are preferred. The distribution of the halogen composition in a grain may be uniform or the halogen composition may be changed stepwise, or it may be changed continuously. Further, a silver halide grain having a core/shell structure can be used preferably. The preferred structure is a twofold to fivefold structure and, more preferably, a core/shell grain having a twofold to fourfold structure can be used. Further, a technique of localizing silver bromide or silver iodide to the surface of silver chloride, silver bromide or silver bromochloride grains can also be used preferably.

[0018]

The distribution of the halogen composition in a grain may be uniform or the halogen composition may be changed stepwise, or it may be changed continuously. Further, a silver halide grain having a core/shell structure can be used preferably. The preferred structure is a twofold to fivefold structure and, more preferably, a core/shell grain having a twofold to fourfold structure can be used. A core-high-silver iodide-structure which has a high content of silver iodide in the core part, and a shell-high-silver iodide-structure which has a high content of silver iodide in the shell part can also be used preferably. Further, a technique of localizing silver bromide or silver iodide to the surface of a grain so as to form an epitaxial part can also be used preferably.

[0019]

### 2) Grain size

The grain size of the photosensitive silver halide is preferably small with an aim of suppressing clouding after image formation and, specifically, it is 0.20  $\mu\text{m}$  or less, more preferably, 0.01  $\mu\text{m}$  to 0.15  $\mu\text{m}$  and, further preferably, 0.02  $\mu\text{m}$  to 0.12  $\mu\text{m}$ . The grain size

as used herein means an average diameter of a circle converted such that it has the same area as a projection area of the silver halide grain (projection area of a principal plane in the case of a tabular grain).

[0020]

3) Coating amount

The addition amount of the photosensitive silver halide, when expressed by the coating amount of silver per one  $\text{m}^2$  of the photosensitive material, is preferably from  $0.03 \text{ g/m}^2$  to  $0.6 \text{ g/m}^2$ , more preferably,  $0.05 \text{ g/m}^2$  to  $0.4 \text{ g/m}^2$  and, further preferably,  $0.07 \text{ g/m}^2$  to  $0.3 \text{ g/m}^2$ . The photosensitive silver halide is used in an amount of 0.001 mol to 0.7 mol, preferably, 0.03 mol to 0.5 mol per one mol of the organic silver salt.

[0021]

4) Method of grain formation

The method of forming photosensitive silver halide is well-known in the relevant art and, for example, methods described in Research Disclosure No. 10729, June 1978 and USP No. 3700458 can be used. Specifically, a method of preparing a photosensitive silver halide by adding a silver-supplying compound and a halogen-supplying compound in a gelatin or other polymer solution and then mixing them with an organic silver salt is used. Further, a method described in Japanese Patent Application Laid-Open (JP-A) No. 11-119374 (paragraph Nos. 0217 to 0224) and methods described in JP-A No. 11-352627 and Japanese Patent Application No. 2000-42336 are also preferred.

[0022]

5) Grain shape

Examples of the shape of the silver halide grain can include, for example, a cubic, octahedral, plate-like, spherical, rod-like or potato-like shape. The cubic grain is particularly preferred in the invention. A silver halide grain rounded at corners can also be used preferably. While there is no particular restriction on the index of plane (Mirror's index) of an crystal surface of the photosensitive silver halide grain, it is preferred that the ratio of [100] face is higher, in which the spectral sensitizing efficiency is higher in a case of adsorption of a spectral sensitizing dye. The ratio is preferably 50% or more, more preferably, 65% or more and, further preferably, 80% or more. The ratio of the Mirror's index [100] face can be determined by the method of utilizing the adsorption dependency of [111] face and [100] face upon adsorption of a sensitizing dye described by T. Tani; in J. Imaging Sci., 29, 165 (1985).

[0023]

6) Heavy metal

The photosensitive silver halide grain of the invention can contain metals or complexes of metals belonging to groups 8 to 10 of the periodical table (showing groups 1 to 18). The metal or the center metal of the metal complex in the groups 8 to 10 of the periodical table is preferably rhodium, ruthenium or iridium. The metal complex may be used alone, or two or more kinds of complexes comprising identical or different species of metals may be used together. A preferred content is within a range from  $1 \times 10^{-9}$  mol to  $1 \times 10^{-3}$  mol per one mol of silver. The heavy metals, metal complexes and the addition method thereof are described in JP-A No. 7-225449, JP-A No. 11-65021 (paragraph Nos. 0018 to 0024) and JP-A No. 11-119374 (paragraph Nos. 0227 to 0240).

[0024]

In the present invention, a silver halide grain having a hexacyano metal complex on

the outermost surface of the grain is preferred. Examples of the hexacyano metal complex include  $[\text{Fe}(\text{CN})_6]^{4-}$ ,  $[\text{Fe}(\text{CN})_6]^{3-}$ ,  $[\text{Ru}(\text{CN})_6]^{4-}$ ,  $[\text{Os}(\text{CN})_6]^{4-}$ ,  $[\text{Co}(\text{CN})_6]^{3-}$ ,  $[\text{Rh}(\text{CN})_6]^{3-}$ ,  $[\text{Ir}(\text{CN})_6]^{3-}$ ,  $[\text{Cr}(\text{CN})_6]^{3-}$ , and  $[\text{Re}(\text{CN})_6]^{3-}$ . In the invention, a hexacyano Fe complex is preferred.

[0025]

Since the hexacyano complex exists in ionic form in an aqueous solution, paired cation is not important and alkali metal ion such as sodium ion, potassium ion, rubidium ion, cesium ion and lithium ion, ammonium ion, alkyl ammonium ion (for example, tetramethyl ammonium ion, tetraethyl ammonium ion, tetrapropyl ammonium ion, and tetra(n-butyl) ammonium ion), which are easily miscible with water and suitable for precipitation operation of a silver halide emulsion are used preferably.

[0026]

The hexacyano metal complex can be added while being mixed with water, as well as a mixed solvent of water and an appropriate organic solvent miscible with water (for example, alcohols, ethers, glycols, ketones, esters and amides) or gelatin.

[0027]

The addition amount of the hexacyano metal complex is preferably from  $1 \times 10^{-5}$  mol to  $1 \times 10^{-2}$  mol and, more preferably, from  $1 \times 10^{-4}$  mol to  $1 \times 10^{-3}$  per one mol of silver in each case.

[0028]

In order to allow the hexacyano metal complex to be present on the outermost surface of a silver halide grain, the hexacyano metal complex is directly added in any stage of: after completion of addition of an aqueous solution of silver nitrate used for grain formation, and before completion of emulsion forming step prior to a chemical sensitization step, of conducting chalcogen sensitization such as sulfur sensitization, selenium sensitization and tellurium sensitization or noble metal sensitization such as gold sensitization; during washing step; during dispersion step; and before chemical sensitization step. In order not to grow the fine silver halide grain, the hexacyano metal complex is rapidly added preferably after the grain is formed, and it is preferably added before completion of the emulsion forming step.

[0029]

Addition of the hexacyano complex may be started after addition of 96 % by mass of an entire amount of silver nitrate to be added for grain formation, more preferably started after addition of 98 % by mass and, particularly preferably, started after addition of 99 % by mass.

When any of the hexacyano metal complexes is added after addition of an aqueous silver nitrate just before completion of grain formation, it can be adsorbed to the outermost surface of the silver halide grain and most of them forms an insoluble salt with silver ions on the surface of the grain. Since the hexacyano iron (II) silver salt is a less soluble salt than AgI, re-dissolution with fine grain can be prevented and fine silver halide grain with smaller grain size can be prepared.

[0030]

Metal atoms that can be contained in the silver halide grain used in the invention, a desalting method of a silver halide emulsion and a chemical sensitization method are described in JP-A No. 11-84574 (paragraph Nos. 0046 to 0050), JP-A No. 11-65021

(paragraph Nos. 0025 to 0031), and JP-A No. 11-119374 (paragraph Nos. 0242 to 0250).

[0031]

7) Gelatin

As the gelatin contained in the photosensitive silver halide emulsion used in the invention, various kinds of gelatins can be used. In order to maintain an excellent dispersion state of a photosensitive silver halide emulsion in an organic silver salt-containing coating solution, low molecular weight gelatin having a molecular weight of 500 to 60,000 is used preferably. The term "molecular weight" as referred to herein means a number-average molecular weight, calculated from styrene-reduced gel permeation chromatography (GPC). These low molecular weight gelatins may be used upon grain formation or at the time of dispersion after desalting treatment, and it is preferably used at the time of dispersion after desalting treatment.

[0032]

8) Chemical sensitization

The photosensitive silver halide in this invention can be used without chemical sensitization, but is preferably chemically sensitized by at least one of chalcogen sensitization method, gold sensitization method and reduction sensitization method. The chalcogen sensitization method includes sulfur sensitization method, selenium sensitization method and tellurium sensitization method.

[0033]

In sulfur sensitization, unstable sulfur compounds can be used. Such unstable sulfur compounds are described in P. Grafkides, *Chimie et Physique Photographique* (Paul Momtel, 1987, 5th ed.) and *Research Disclosure* (Vol. 307, Item 307105), and the like.

As typical examples of sulfur sensitizer, known sulfur compounds such as thiosulfates (e.g., hypo), thioureas (e.g., diphenylthiourea, triethylthiourea, N-ethyl-N'-(4-methyl-2-thiazolyl)thiourea and carboxymethyltrimethylthiourea), thioamides (e.g., thioacetamide), rhodanines (e.g., diethylrhodanine, 5-benzylidene-N-ethylrhodanine), phosphinesulfides (e.g., trimethylphosphinesulfide), thiohydantoins, 4-oxo-oxazolidin-2-thione derivatives, disulfides or polysulfides (e.g., dimorphorinedisulfide, cystine, hexathiocane-thione), polythionates, sulfur element and active gelatin can be used. Specifically, thiosulfates, thioureas and rhodanines are preferred.

[0034]

In selenium sensitization, unstable selenium compounds can be used. These unstable selenium compounds are described in JP-B Nos. 43-13489 and 44-15748, JP-A Nos. 4-25832, 4-109340, 4-271341, 5-40324, and 5-11385, Japanese Patent Application Nos. 4-202415, 4-330495, 4-333030, 5-4203, 5-4204, 5-106977, 5-236538, 5-241642, and 5-286916, and the like.

[0035]

As typical examples of selenium sensitizer, colloidal metal selenide, selenoureas (e.g., N,N-dimethylselenourea, trifluoromethylcarbonyl-trimethylselenourea and acetyltrimethylselenourea), selenamides (e.g., selenamide and N,N-diethylphenylselenamide), phosphineselenides (e.g., triphenylphosphineselenide and pentafluorophenyl-triphenylphosphineselenide), selenophosphates (e.g., tri-p-tolylselenophosphate and tri-n-butylselenophosphate), selenoketones (e.g., selenobenzophenone), isoselenocyanates, selenocarbonic acids, selenoesters, diacylselenides



can be used. Furthermore, non-unstable selenium compounds such as selenious acid, selenocyanic acid, selenazoles and selenides described in JP-B Nos. 46-4553 and 52-34492 can also be used. Specifically, phosphineselenides, selenoureas and salts of selenocyanic acids are preferred.

[0036]

In the tellurium sensitization, unstable tellurium compounds are used. Unstable tellurium compounds described in JP-A Nos. 4-224595, 4-271341, 4-333043, 5-303157, 6-27573, 6-175,258, 6-180478, 6-208186, 6-208184, 6-317867, 7-140579, 7-301879, 7-301880 and the like, can be used as tellurium sensitizers.

[0037]

As typical examples of tellurium sensitizer, phosphinetellurides (e.g., butyl-diisopropylphosphinetelluride, tributylphosphinetelluride, tributoxyphosphinetelluride and ethoxy-diphenylphosphinetelluride), diacyl(di)tellurides (e.g., bis(diphenylcarbamoyl)ditelluride, bis(N-phenyl-N-methylcarbamoyl)ditelluride, bis(N-phenyl-N-methylcarbamoyl)ditelluride, bis(N-phenyl-N-benzylcarbamoyl)telluride and bis(ethoxycarbonyl)telluride), telluroureas (e.g., N,N'-dimethylethylenetellurourea and N,N'-diphenylethylenetellurourea), telluramides, telluroesters are used. Specifically, diacyl(di)tellurides and phosphinetellurides are preferred. Especially, the compounds described in paragraph No. 0030 in JP-A No. 11-65021 and compounds represented by the general formulae [II], [III] and [IV] in JP-A No. 5-313284 are more preferred.

[0038]

Selenium sensitization and tellurium sensitization are preferred as chalcogen sensitization and specifically, tellurium sensitization is more preferred.

[0039]

In gold sensitization, gold sensitizer described in P. Grafkides, *Chimie et Physique Photographique* (Paul Momtel, 1987, 5th ed.) and *Research Disclosure* (Vol. 307, Item 307105) can be used. To speak concretely, chloroauric acid, potassium chloroaurate, potassium aurithiocyanate, gold sulfide, gold selenide and the like can be used. In addition to these, the gold compounds described in U.S. Patent Nos. 2642361, 5049484, 5049485, 5169751, and 5252455, Belg. Patent No. 691857, and the like can also be used. And other novel metal salts except gold such as platinum, palladium, iridium and so on described in P. Grafkides, *Chimie et Physique Photographique* (Paul Momtel, 1987, 5th ed.) and *Research Disclosure* (Vol. 307, Item 307105) can be used.

[0040]

The gold sensitization can be used independently. But it is preferably used in combination with the above chalcogen sensitization. To speak specifically, these sensitizations are gold-sulfur sensitization (gold-plus-sulfur sensitization), gold-selenium sensitization, gold-tellurium sensitization, gold-sulfur-selenium sensitization, gold-sulfur-tellurium sensitization, gold-selenium-tellurium sensitization and gold-sulfur-selenium-tellurium sensitization.

[0041]

In the invention, chemical sensitization can be applied at any time so long as it is after grain formation and before coating, and it can be applied, after desalting, (1) before spectral sensitization, (2) simultaneously with spectral sensitization, (3) after spectral

sensitization and (4) just before coating.

[0042]

The amount of chalcogen sensitizer used in the invention may vary depending on the silver halide grain used, the chemical ripening condition and the like and it is used in amount of about  $10^{-8}$  mol to  $10^{-1}$  mol, preferably,  $10^{-7}$  mol to  $10^{-2}$  mol per one mol of the silver halide.

Similarly, the addition amount of the gold sensitizer used in the invention may vary depending on various conditions and it is generally about  $10^{-7}$  mol to  $10^{-3}$  mol and, more preferably,  $10^{-6}$  mol to  $5 \times 10^{-3}$  mol per one mol of the silver halide. There is no particular restriction on the condition for the chemical sensitization in the invention and, appropriately, pAg is 8 or less, preferably, 7.0 or less, more preferably, 6.5 or less and, particularly preferably, 6.0 or less, and pAg is 1.5 or more, preferably, 2.0 or more, particularly preferable, 2.5 or more, pH is 3 to 10, preferably, 4 to 9, and temperature is at 20°C to 95°C, preferably, 25°C to 80°C.

[0043]

In the invention, reduction sensitization can also be used in combination with the chalcogen sensitization or the gold sensitization. It is specifically preferred to use in combination with the chalcogen sensitization.

As the specific compound for the reduction sensitization, ascorbic acid, thiourea dioxide or dimethylamine borane is preferred, as well as use of stannous chloride, aminoimino methane sulfonic acid, hydrazine derivatives, borane compounds, silane compounds and polyamine compounds is preferred. The reduction sensitizer may be added at any stage in the photosensitive emulsion production process from crystal growth to the preparation step just before coating. Further, it is preferred to apply reduction sensitization by ripening while keeping pH to 8 or higher and pAg to 4 or lower for the emulsion, and it is also preferred to apply reduction sensitization by introducing a single addition portion of silver ions during grain formation.

The addition amount of the reduction sensitizer may also vary depending on various conditions and it is generally about  $10^{-7}$  mol to  $10^{-1}$  mol and, more preferably,  $10^{-6}$  mol to  $5 \times 10^{-2}$  mol per one mol of the silver halide.

[0044]

In the silver halide emulsion used in the invention, a thiosulfonic acid compound may be added by the method shown in EP-A No. 293917.

The photosensitive silver halide grain in the invention can be chemically unsensitized, but is preferably chemically sensitized by at least one method of gold sensitization method and chalcogen sensitization method for the purpose of designing a high-photosensitive photothermographic material.

[0045]

#### 9) FED sensitizer

The photosensitive silver halide emulsion in the invention preferably contains an FED sensitizer (Fragmentable Electron Donating Sensitizer) as a compound generating two electrons by one photon. As the FED sensitizer, those compounds described in USP Nos. 5747235, 5747236, 6054260 and 5994051, and Japanese Patent Application No. 2001-86161 are preferred. The FED sensitizer may be added preferably at any stage in the photosensitive emulsion production process from the crystal growth to the preparation step just before coating. The addition amount may vary depending on various conditions and as a standard, it is about from  $10^{-7}$  mol to  $10^{-1}$  mol, more preferably,  $10^{-6}$  mol to  $5 \times 10^{-2}$  mol per one mol of

the silver halide.

[0046]

10) Sensitizing dye

As the sensitizing dye applicable in the invention, those capable of spectrally sensitizing silver halide grains in a desired wavelength region upon adsorption to silver halide grains having spectral sensitivity suitable for spectral characteristics of an exposure light source can be selected advantageously. The photothermographic material of the present invention is preferably spectrally sensitized by sensitizers having a maximum spectral sensitivity of 600 nm to 900 nm or 300 nm to 500 nm. The sensitizing dyes and the addition method are disclosed, for example, in JP-A No. 11-65021 (paragraph Nos. 0103 to 0109), a compound represented by the general formula (II) in JP-A No. 10-186572, dyes represented by the general formula (I) in JP-A No. 11-119374 (paragraph No. 0106), dyes described in USP Nos. 5510236 and 3871887 (Example 5), dyes disclosed in JP-A Nos. 2-96131 and 59-48753, as well as page 19, line 38 to page 20, line 35 of EP-A No. 0803764A1, and in Japanese Patent Application Nos. 2000-86865, 2000-102560 and 2000-205399. The sensitizing dyes described above may be used alone or two or more of them may be used in combination. The sensitizing dye is added into the silver halide emulsion preferably within a period after desalting step to coating step and, more preferably, in a period after desalting to the completion of chemical ripening.

[0047]

In the invention, the sensitizing dye may be added at any amount according to the property of photosensitivity and fogging, but it is preferably added from  $1 \times 10^{-6}$  mol to 1 mol, and more preferably, from  $1 \times 10^{-4}$  mol to  $1 \times 10^{-1}$  mol per one mol of silver in each case.

[0048]

A supersensitizer can be used in the invention in order to improve spectral sensitization efficiency. Examples of the supersensitizer include compounds described in EP-A No. 587338, U.S. Patent Nos. 3877493 and 4873184, and JP-A Nos. 5-341432, 11-109547 and 10-111543.

[0049]

11) Combined use of a plurality of silver halides

The photosensitive silver halide emulsion in the photothermographic material used in the invention may be used alone, or two or more kinds of them (for example, those of different average particle sizes, different halogen compositions, different crystal habits and of different conditions for chemical sensitization) may be used together. Gradation can be controlled by using plural kinds of photosensitive silver halides of different sensitivity. The relevant techniques can include those described, for example, in JP-A Nos. 57-119341, 53-106125, 47-3929, 48-55730, 46-5187, 50-73627, and 57-150841. It is preferred to provide a sensitivity difference of 0.2 logE or more between each of the emulsions.

[0050]

12) Mixing silver halide and organic silver salt

The photosensitive silver halide in the invention is particularly preferably formed in the absence of the non-photosensitive organic silver salt and then mixed in the process for preparing the organic silver salt. This is because a sufficient sensitivity can not sometimes be attained by the method of forming the silver halide by adding a halogenating agent to the organic silver salt.

Examples of the method of mixing the silver halide and the organic silver salt include a method of mixing a separately prepared photosensitive silver halide and an organic silver salt by a high speed stirrer, ball mill, sand mill, colloid mill, vibration mill, or homogenizer, or a method of mixing a photosensitive silver halide completed for preparation at any timing in the preparation of an organic silver salt and preparing the organic silver salt. The effect of the invention can be obtained preferably by any of the methods described above.

[0051]

13) Mixing silver halide into coating solution

In the invention, the time of adding silver halide to the coating solution for the image forming layer is preferably in the range from 180 minutes before to just prior to the coating, more preferably, 60 minutes before to 10 seconds before coating. But there is no restriction on mixing methods and mixing conditions as far as the effect of the invention appears sufficient. As an embodiment of a mixing method, there is a method of mixing in the tank controlling the average residence time desired. The average residence time herein is calculated from addition flux and the amount of solution transferred to the coater. Another embodiment of mixing method is a method using a static mixer, which is described in 8th edition of "Ekitai kongou gijutu" by N. Harnby and M. F. Edwards, translated by Kouji Takahashi (Nikkankougyou shinbunsha, 1989).

[0052]

3. Non-photosensitive organic silver salt

1) Composition

The non-photosensitive organic silver salt particle (hereinafter may be referred to simply as the "organic silver salt") according to the invention is relatively stable to light but forms silver images when heated to 80°C or higher in the presence of an exposed photocatalyst (such as a latent image of photosensitive silver halide) and a reducing agent.

The organic silver salt may be any organic material containing a source capable of reducing silver ions. Such non-photosensitive organic silver salt is disclosed, for example, in JP-A Nos. 6-130543, 8-314078, 9-127643, 10-62899 (paragraph Nos. 0048 to 0049), 10-94074, and 10-94075, EP-A No. 0803764A1 (page 18, line 24 to page 19, line 37), EP-A Nos. 962812A1 and 1004930A2, and JP-A Nos. 11-349591, 2000-7683, 2000-72711, 2000-112057 and 2000-155383.

A silver salt of organic acid, particularly, a silver salt of long chain aliphatic carboxylic acid (having 10 to 30, preferably 15 to 28 carbon atoms) is preferable as the non-photosensitive organic silver salt of the invention. Preferred examples of the silver salt of the organic acid can include silver behenate, silver arachidinic acid, silver stearate, silver oleate, silver laurate, silver capronate, silver myristate, silver palmitate and mixtures thereof. Among the organic silver salts, it is preferred to use an organic silver salt with a silver behenate content of 30 mol% to 90 mol%, and more preferably 40 mol% to 70 mol%. Another preferred example of the organic silver salt is a silver salt of long chain aliphatic carboxylic acid having 10 to 30, preferably 15 to 28 carbon atoms.

[0053]

2) Shape

Although there is no particular restriction on the shape of the organic silver salt, the organic silver salt in the form of a needle crystal having a major axis and a minor axis is preferable. It is well-known in the field of silver halide photographic photosensitive materials that the size of the silver salt crystal grain is inversely proportional to covering power thereof. This relationship applies to the photothermographic material of the invention

as well. Namely, the larger the size of the organic silver particles which are image forming components of the photothermographic material, the lower the covering power and the density of the resulting image. Thus, it is preferable to make the organic silver salt particles small. In the present invention, organic silver salt particles having a minor axis of 0.01  $\mu\text{m}$  to 0.15  $\mu\text{m}$  and a major axis of 0.10  $\mu\text{m}$  to 5.0  $\mu\text{m}$ , preferably a minor axis of 0.01  $\mu\text{m}$  to 0.15  $\mu\text{m}$  and a major axis of 0.10  $\mu\text{m}$  to 4.0  $\mu\text{m}$ , are used.

[0054]

As the particle size distribution of the organic silver salt, mono-dispersion is preferred. In the mono-dispersion, the percentage for the value obtained by dividing the standard deviation for the length of the minor axis and the major axis by the minor axis and the major axis, respectively, is preferably 100% or less, more preferably 80% or less, and further preferably 50% or less.

[0055]

### 3) Preparation...

#### 3-1) Preparation of organic silver salt for addition to organic solvent

In a case of preparing a coating solution by adding the organic silver salt to an organic solvent, it is important that the previously prepared photosensitive silver halide is mixed in the step of preparing the organic silver salt to prepare a dispersion of an organic silver salt containing the silver halide. The organic silver salt is prepared by mixing an organic acid or an alkali metal salt thereof with a water soluble silver salt (for example, silver nitrate). The silver halide can be added at any of the stages thereof. Main mixing step can include three steps comprising: (A) adding a silver halide previously to an organic acid and, after addition of an alkali metal salt, mixing with a water soluble silver salt, (B) forming a portion of an organic acid or an alkali metal salt thereof into a silver salt, then mixing a silver halide and, subsequently, forming a silver salt for the remaining portion and (C) mixing a silver halide in the subsequent step after completion of an organic silver salt. The steps (B) and (C) are preferred, with the step (B) being particularly preferred.

[0056]

All of those salt forming steps are carried out in an aqueous solvent and then the salt is dewatered, dried and then re-dispersed into a solvent such as MEK. Drying is preferably conducted in an airflow-type flash jet drier at a partial oxygen pressure of 15 vol% or less, more preferably, at 0.01 vol% to 15 vol% and, more preferably, at 0.01 vol% to 10 vol%.

[0057]

Although the organic silver salt may be used in any desired amount, the coating amount of the organic silver salt is 0.1 to 5  $\text{g/m}^2$ , and preferably 1 to 3  $\text{g/m}^2$ .

[0058]

#### 3-2) Preparation of organic silver salt for addition to water solvent

In a case of using water as the solvent to prepare a coating solution, known methods can be applied. For example, reference can be made to JP-A No. 10-62899, EP-A Nos. 0803763A1 and 0962812A1, JP-A Nos. 11-349591, 2000-7683, 2000-72711, 2001-163889, 2001-163890, 2001-163827, 2001-33907, 2001-188313, 2001-83652, 2002-6442, 2002-49117, 2002-31870 and 2002-107868.

[0059]

When a photosensitive silver salt is present during dispersion of the organic silver

salt, fog increases and the sensitivity becomes remarkably lower, so it is more preferred that the photosensitive silver salt is not substantially contained during dispersion. In the invention, the amount of the photosensitive silver salt to be dispersed in the aqueous dispersion is preferably 1 mol% or less, more preferably, 0.1 mol% or less per one mol of the organic acid silver salt in the solution and, further preferably, positive addition of the photosensitive silver salt is not conducted.

[0060]

In the invention, the photosensitive material can be prepared by mixing an aqueous dispersion of an organic silver salt and an aqueous dispersion of a photosensitive silver salt and the mixing ratio between the organic silver salt and the photosensitive silver salt can be selected depending on the purpose. The ratio of the photosensitive silver salt to the organic silver salt is, preferably, within a range from 1 mol% to 30 mol%, more preferably, within a range from 2 mol% to 20 mol% and, particularly preferably, 3 mol% to 15 mol%. A method of mixing two or more kinds of aqueous dispersions of organic silver salts and two or more kinds of aqueous dispersions of photosensitive silver salts upon mixing is used preferably for controlling the photographic properties.

[0061]

#### 4. Reducing agent

The photothermographic material of the invention contains a reducing agent for the organic silver salt. The reducing agent may be any substance (preferably, organic substance) capable of reducing silver ions into metallic silver. Examples of the reducing agent are described in JP-A No. 11-65021 (paragraph Nos. 0043 to 0045) and EP-A 0803764 (p.7, line 34 to p. 18, line 12).

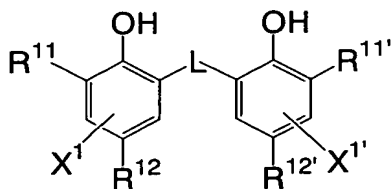
[0062]

In the invention, a so-called hindered phenolic reducing agent or a bisphenol agent having a substituent at the ortho-position to the phenolic hydroxyl group is preferred, and the bisphenolic reducing agent is more preferred. Particularly, the compound represented by the following general formula (R) is preferred.

[0063]

General formula (R)

[Formula 1]



[0064]

In the general formula (R),  $R^{11}$  and  $R^{11'}$  each independently represent an alkyl group having 1 to 20 carbon atoms.  $R^{12}$  and  $R^{12'}$  each independently represents a hydrogen atom or a group capable of substituting for a hydrogen atom on a benzene ring.  $L$  represents a -S- group or a -CHR<sup>13</sup>- group.  $R^{13}$  represents a hydrogen atom or an alkyl group having 1 to 20 carbon atoms.  $X$  and  $X^1$  each independently represents a hydrogen atom or a group capable of substituting for a hydrogen atom on a benzene ring.

[0065]

Each of the substituents is to be described specifically.

1)  $R^{11}$  and  $R^{11'}$

$R^{11}$  and  $R^{11'}$  each independently represents a substituted or unsubstituted alkyl group having 1 to 20 carbon atoms. The substituent for the alkyl group has no particular restriction, and examples thereof can include, preferably, aryl group, hydroxy group, alkoxy group, aryloxy group, alkylthio group, arylthio group, acylamino group, sulfoneamide group, sulfonyl group, phosphoryl group, acyl group, carbamoyl group, ester group, and a halogen atom.

[0066]

2)  $R^{12}$  and  $R^{12'}$ , X and  $X^1$

$R^{12}$  and  $R^{12'}$  each independently represent a hydrogen atom or a group capable of substituting for a hydrogen atom on a benzene ring.

X and  $X^1$  each independently represent a hydrogen atom or a group capable of substituting for a hydrogen atom on a benzene ring. Examples of the groups capable of substituting for a hydrogen atom on the benzene ring can include, preferably, alkyl group, aryl group, halogen atom, alkoxy group, and acylamino group.

[0067]

3) L

L represents a -S- group or a -CHR<sup>13</sup>- group.  $R^{13}$  represents a hydrogen atom or an alkyl group having 1 to 20 carbon atoms in which the alkyl group may have a substituent.

Specific examples of the non-substituted alkyl group for  $R^{13}$  can include methyl group, ethyl group, propyl group, butyl group, heptyl group, undecyl group, isopropyl group, 1-ethylpentyl group, and 2,4,4-trimethylpentyl group.

[0068]

Examples of the substituent for the alkyl group can include, like the substituent  $R^{11}$ , a halogen atom, an alkoxy group, alkylthio group, aryloxy group, arylthio group, acylamino group, sulfoneamide group, sulfonyl group, phosphoryl group, oxycarbonyl group, carbamoyl group, and sulfamoyl group.

[0069]

4) Preferred substituents

$R^{11}$  and  $R^{11'}$  are, preferably, a secondary or tertiary alkyl group having 3 to 15 carbon atoms, and specific examples thereof include isopropyl group, isobutyl group, t-butyl group, t-amyl group, t-octyl group, cyclohexyl group, cyclopentyl group, 1-methylcyclohexyl group, and 1-methylcyclopropyl group.  $R^{11}$  and  $R^{11'}$  each represent, more preferably, tertiary alkyl group having 4 to 12 carbon atoms and, among them, t-butyl group, t-amyl group, 1-methylcyclohexyl group are further preferred, and t-butyl group is most preferred.

[0070]

$R^{12}$  and  $R^{12'}$  are, preferably, alkyl groups having 1 to 20 carbon atoms, and specific examples thereof include methyl group, ethyl group, propyl group, butyl group, isopropyl group, t-butyl group, t-amyl group, cyclohexyl group, 1-methylcyclohexyl group, benzyl group, methoxymethyl group and methoxyethyl group. More preferred are methyl group, ethyl group, propyl group, isopropyl group, and t-butyl group.

[0071]

X and X<sup>1</sup> are, preferably, a hydrogen atom, halogen atom, or alkyl group, and more preferably, hydrogen atom.

[0072]

L is preferably a -CHR<sup>13</sup>- group.

[0073]

R<sup>13</sup> is, preferably, a hydrogen atom or an alkyl group having 1 to 15 carbon atoms. The alkyl group is preferably methyl group, ethyl group, propyl group, isopropyl group and 2,4,4-trimethylpentyl group. Particularly preferred R<sup>13</sup> is a hydrogen atom, methyl group, propyl group or isopropyl group.

[0074]

In a case where R<sup>13</sup> is a hydrogen atom, R<sup>12</sup> and R<sup>12'</sup> each represent, preferably, an alkyl group having 2 to 5 carbon atoms, ethyl group and propyl group being more preferred and ethyl group being most preferred.

[0075]

In a case where R<sup>13</sup> is a primary or secondary alkyl group having 1 to 8 carbon atoms, R<sup>12</sup> and R<sup>12'</sup> each represent preferably methyl group. As the primary or secondary alkyl group of 1 to 8 carbon atoms for R<sup>13</sup>, methyl group, ethyl group, propyl group and isopropyl group are more preferred, and methyl group, ethyl group, and propyl group are further preferred.

[0076]

In a case where each of R<sup>11</sup>, R<sup>11'</sup> and R<sup>12</sup>, R<sup>12'</sup> is methyl group, R<sup>13</sup> is preferably a secondary alkyl group. In this case, the secondary alkyl group for R<sup>13</sup> is preferably isopropyl group, isobutyl group and 1-ethylpentyl group, with isopropyl group being more preferred.

[0077]

The reducing agent described above show various different thermo-developing performance depending on the combination of R<sup>11</sup>, R<sup>11'</sup> and R<sup>12</sup>, R<sup>12'</sup>, as well as R<sup>13</sup>. Since the thermo-developing performances can be controlled by using two or more kinds of reducing agents at various mixing ratios, it is preferred to use two or more kinds of reducing agents in combination depending on the purpose.

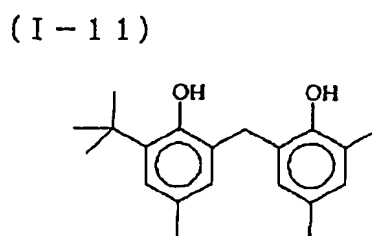
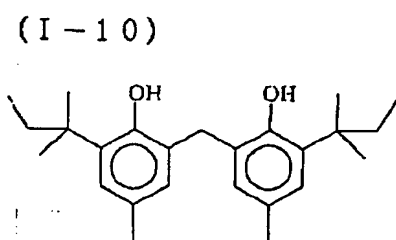
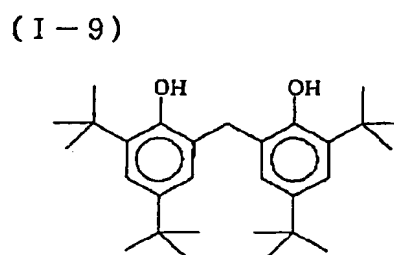
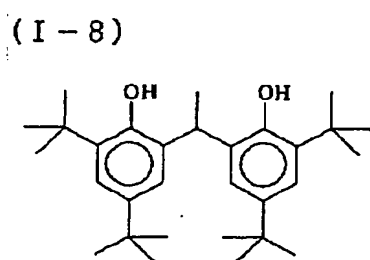
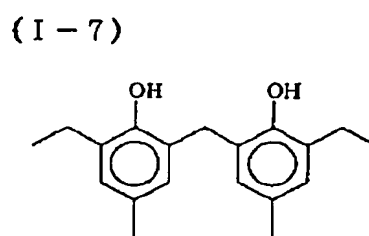
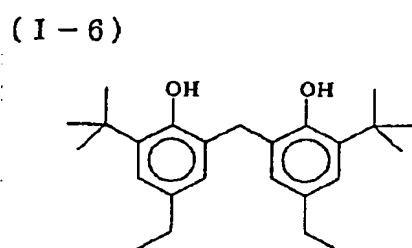
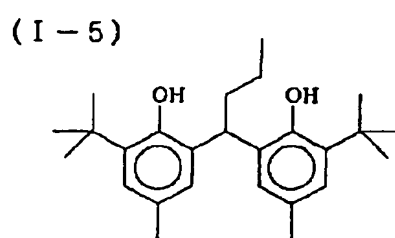
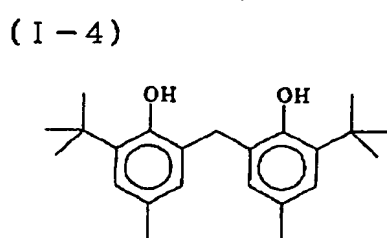
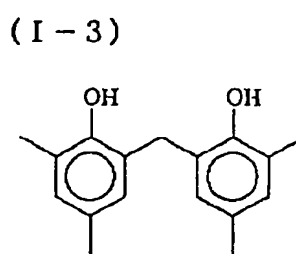
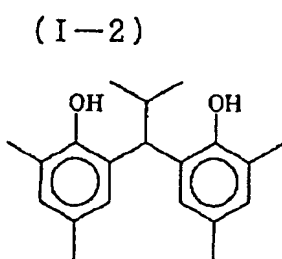
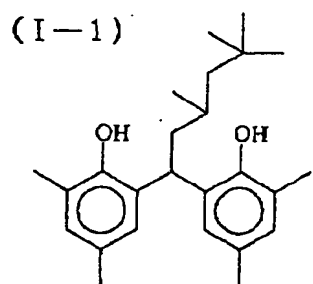
[0078]

Specific examples of the compounds represented by general formula (R) according to the invention are shown below but the invention is not restricted to them.

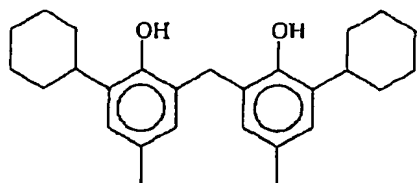
[0079]

[Formula 2]

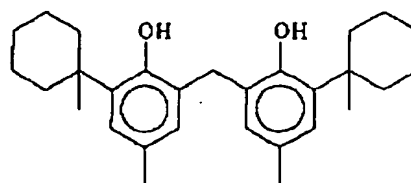




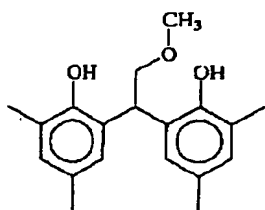
(I-12)



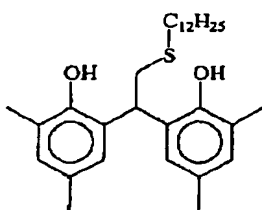
(I-13)



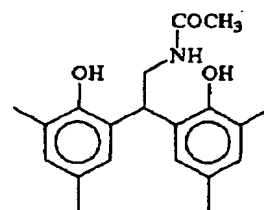
(I-14)



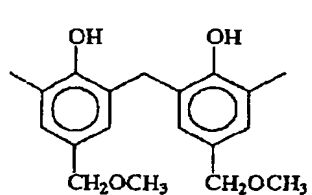
(I-15)



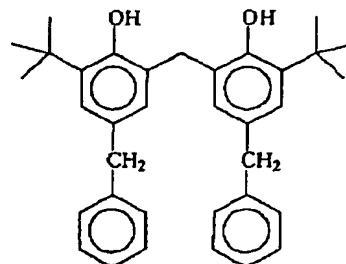
(I-16)



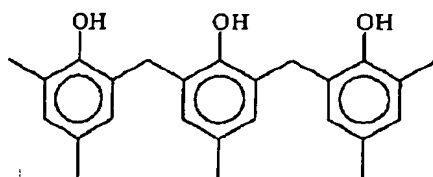
(I-17)



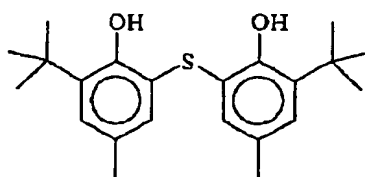
(I-18)



(I-19)



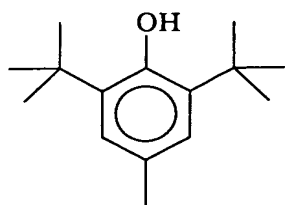
(I-20)



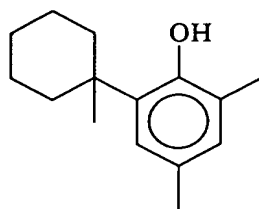
[0081]

[Formula 4]

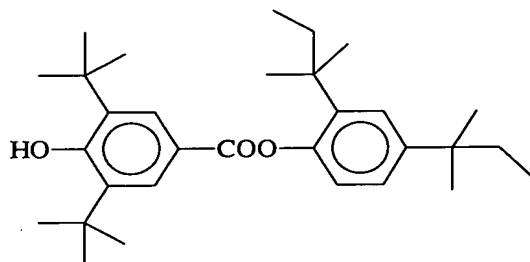
( I - 2 1 )



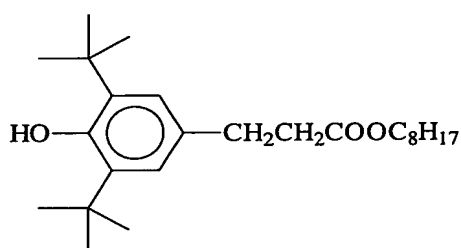
( I - 2 2 )



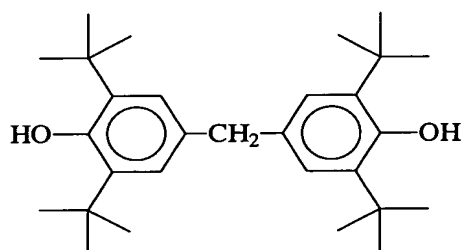
( I - 2 3 )



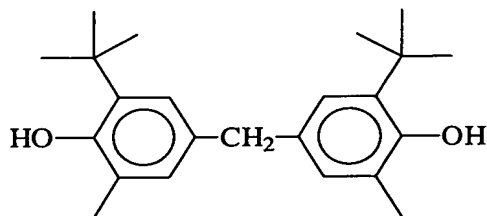
( I - 2 4 )



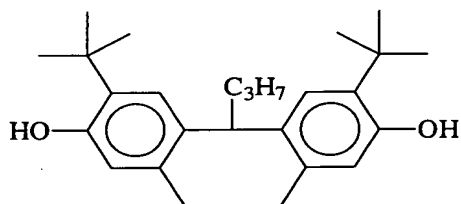
( I - 2 5 )



( I - 2 6 )



( I - 2 7 )



[0082]

In the invention, the addition amount of the reducing agent is, preferably, from 0.01 g/m<sup>2</sup> to 5.0 g/m<sup>2</sup>, more preferably, 0.1 g/m<sup>2</sup> to 3.0 g/m<sup>2</sup>. It is, preferably, contained in an amount of 5 mol% to 50 mol% , more preferably, 10 mol% to 40 mol% per mol of silver in the image forming layer.

[0083]

The reducing agent of the invention can be added to an image forming layer containing the organic silver salt and the photosensitive silver halide, and a layer adjacent to the image forming layer. However, the reducing agent is more preferably contained in the image forming layer.

[0084]

In the invention, the reducing agent may be incorporated into photosensitive material by being added into the coating solution, such as in the form of a solution, an emulsion dispersion, a solid particle dispersion, and the like. Preferably, the reducing agent is incorporated into the photosensitive material by being dissolved in a coating solvent.

[0085]

#### 6. Antifoggant

In the photothermographic material of the present invention, the silver halide emulsion and/or the organic silver salt can further be protected by an antifoggant, a stabilizer and a stabilizer precursor from generation of additional fogging, and can be stabilized against decreases in the sensitivity during storage. Examples of the antifoggant, the stabilizer and the stabilizer precursor which can be used alone or in combination include thiazonium salts described in U.S. Patent Nos. 2131038 and 2694716, azaindene described in U.S. Patent Nos. 2886437 and 2444605, compounds described in JP-A No. 9-329865 and U.S. Patent No. 6083681, mercury salt described in U.S. Patent No. 2728663, urazole described in U.S. Patent No. 3287135, sulfocatechol described in U.S. Patent No. 3235652, oxime, nitron and nitroindazole described in UK Patent No. 623448, polyvalent metal salt described in U.S. Patent No. 2839405, thiuronium salt described in U.S. Patent No. 3220839, palladium, platinum and gold salt described in U.S. Patent Nos. 2566263 and 2597915, halogen-substituted organic compounds described in U.S. Patent Nos. 4108665 and 4442202, triazine described in U.S. Patent Nos. 4128557, 4137079, 4138365 and 4459350, and a phosphor compound described in U.S. Patent No. 4411985.

[0086]

Organic halogen compounds are preferable as the antifoggant. Polyhalomethyl compounds, particularly a trihalomethyl sulfone compound, are more preferable. Further, the antifoggant is preferably a compound expressed by general formula (PO) below:

General formula (PO) :  $Q-(Y)_n-C(Z_1)(Z_2)X$

In general formula (PO), Q represents a heterocyclic group; Y represents a divalent connecting group; n represents 0 or 1;  $Z_1$  and  $Z_2$  represent a halogen atom; and X represents a hydrogen atom or an electron attracting group.

[0087]

In general formula (H), Q is preferably an aryl group or a heterocyclic group.

Q preferably is a nitrogen-containing heterocyclic group having 1 or 2 nitrogen atoms, and particularly preferred are 2-pyridyl group and 2-quinolyl group.

[0088]

X preferably is an electron-attracting group, more preferably, a halogen atom, an aliphatic aryl or heterocyclic sulfonyl group, an aliphatic aryl or heterocyclic acyl group, an aliphatic aryl or heterocyclic oxycarbonyl group, carbamoyl group, or sulfamoyl group; particularly preferred among them is a halogen atom. Among halogen atoms, preferred are chlorine atom, bromine atom, and iodine atom; more preferred are chlorine atom and bromine atom; and particularly preferred is bromine atom.

[0089]

Y preferably represents  $-C(=O)-$ ,  $-SO-$ , or  $-SO_2-$ ; more preferably,  $-C(=O)-$  or  $-SO_2-$ ; and particularly preferred is  $-SO_2-$ . n represents 0 or 1, and preferred is 1.

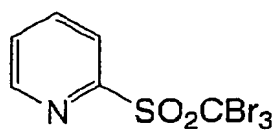
[0090]

Specific examples of the compound expressed by general formula (H) of the invention are shown below but are not limited to them.

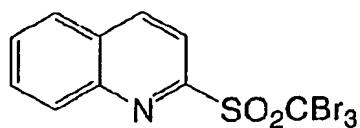
[0091]

[Formula 5]

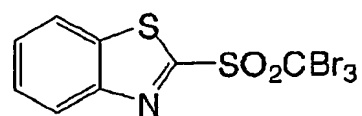
(P0-1)



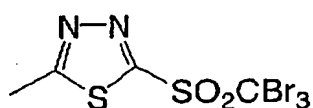
(P0-2)



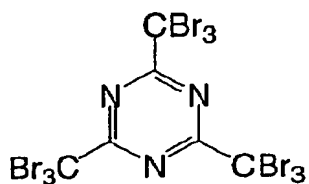
(P0-3)



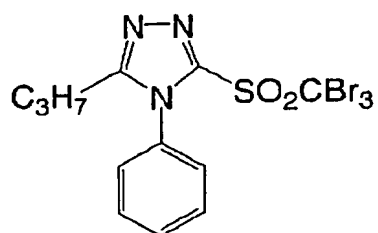
(P0-4)



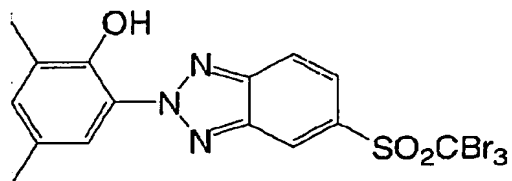
(P0-5)



(P0-6)



(P0-7)



[0092]

The compounds expressed by general formula (PO) of the invention are preferably used in an amount of from  $10^{-4}$  mol to 1 mol, more preferably,  $10^{-3}$  mol to 0.5 mol, and most preferably,  $1 \times 10^{-2}$  mol to 0.2 mol, per one mol of non-photosensitive silver salt incorporated in the image forming layer.

[0093]

#### 6. Development accelerator

A development accelerator is preferably added to the photothermographic material of the invention. Examples of the development accelerator include sulfoneamide phenolic compounds represented by the general formula (A) described in the specification of JP-A No. 2000-267222, and specification of JP-A No. 2000-330234, hindered phenolic compound represented by the general formula (II) described in JP-A No. 2001-92075, hydrazine series compounds represented by general formula (I) described in the specification of JP-A No. 10-62895 and the specification of JP-A No. 11-15116, and represented by general formula (1) described in the specification of Japanese Patent Application No. 2001-074278, and phenolic or naphthalic compounds represented by general formula (2) described in the specification of JP-A No. 2001-264929 are used preferably as the development accelerator and they are added preferably. The development accelerator described above is used within a range from 0.1 mol% to 20 mol%, preferably, within a range from 0.5 mol% to 10 mol% and, more preferably, within a range from 1 mol% to 5 mol% to the reducing agent. Examples of the introduction method to the photothermographic material can include the same method as those for the reducing agent, and it is particularly preferred to add the development accelerator to the photothermographic material in the form of a solution.

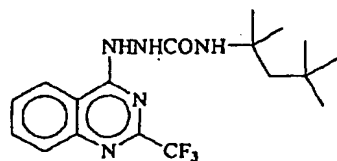
In the present invention, it is more preferred to use, among the development accelerators described above, hydrazine compounds represented by general formula (1) described in the specification of JP-A No. 2001-074278, and naphtholic compounds represented by general formula (2) described in the specification of JP-A No. 2001-264929.

Specific examples of preferred development accelerators of the invention are shown below. The invention, however, is not limited to these examples.

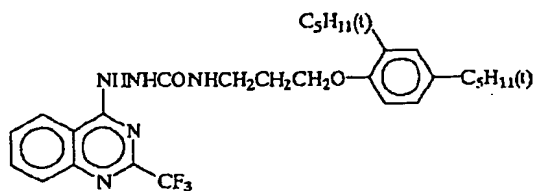
[0094]

[Formula 6]

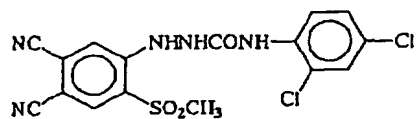
(A-1)



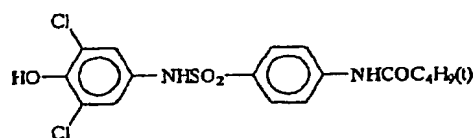
(A-2)



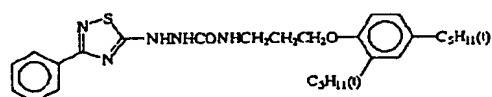
(A-3)



(A-4)



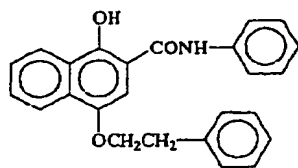
(A-5)



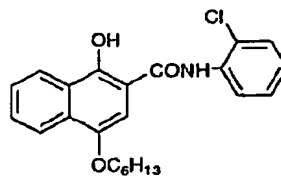
(A-6)



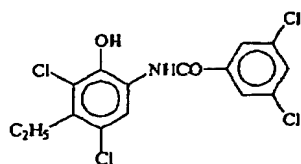
(A-7)



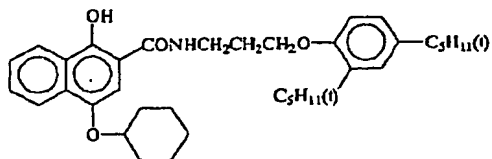
(A-8)



(A-9)



(A-10)



[0095]

7. Hydrogen bonding compound

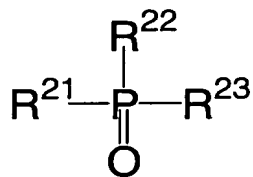
In the invention, it is preferred to use in combination, a non-reducing compound having a group capable of reacting with an aromatic hydroxyl group (-OH) of the reducing agent group, and that is also capable of forming a hydrogen bond therewith. As a group forming a hydrogen bond with a hydroxyl groups, there can be mentioned a phosphoryl group, a sulfoxido group, a sulfonyl group, a carbonyl group, an amido group, an ester group, an urethane group, an ureido group, a tertiary amino group, a nitrogen-containing aromatic group, and the like. Particularly preferred among them is phosphoryl group, sulfoxido group, amido group (not having >N-H moiety but being blocked in the form of >N-Ra (where, Ra represents a substituent other than H)), urethane group (not having >N-H moiety but being blocked in the form of >N-Ra (where, Ra represents a substituent other than H)), and ureido group (not having >N-H moiety but being blocked in the form of >N-Ra (where, Ra represents a substituent other than H)).

In the invention, particularly preferred as the hydrogen-bonding compound is the compound expressed by general formula (D) shown below.

General formula (D)

[0096]

[Formula 7]



[0097]

In general formula (D),  $\text{R}^{21}$  to  $\text{R}^{23}$  each independently represent an alkyl group, an aryl group, an alkoxy group, an aryloxy group, an amino group, or a heterocyclic group, which may be substituted or not substituted. In the case  $\text{R}^{21}$  to  $\text{R}^{23}$  contain a substituent, examples of the substituents include a halogen atom, an alkyl group, an aryl group, an alkoxy group, an amino group, an acyl group, an acylamino group, an alkylthio group, an arylthio group, a sulfonamido group, an acyloxy group, an oxycarbonyl group, a carbamoyl group, a sulfamoyl group, a sulfonyl group, a phosphoryl group, and the like, in which preferred as the substituents are an alkyl group or an aryl group, e.g., methyl group, ethyl group, isopropyl group, t-butyl group, t-octyl group, phenyl group, a 4-alkoxyphenyl group, a 4-acyloxyphenyl group, and the like.

Specific examples of an alkyl group expressed by  $\text{R}^{21}$  to  $\text{R}^{23}$  include methyl group, ethyl group, butyl group, octyl group, dodecyl group, isopropyl group, t-butyl group, t-amyl group, t-octyl group, cyclohexyl group, 1-methylcyclohexyl group, benzyl group, phenetyl group, 2-phenoxypropyl group, and the like. As aryl groups, there can be mentioned phenyl group, cresyl group, xylyl group, naphthyl group, 4-t-butylphenyl group, 4-t-octylphenyl group, 4-anisidyl group, 3,5-dichlorophenyl group, and the like. As alkoxy groups, there can be mentioned methoxy group, ethoxy group, butoxy group, octyloxy group, 2-ethylhexyloxy group, 3,5,5-trimethylhexyloxy group, dodecyloxy group, cyclohexyloxy group, 4-methylcyclohexyloxy group, benzyloxy group, and the like. As aryloxy groups, there can be mentioned phenoxy group, cresyloxy group, isopropylphenoxy group, 4-t-butylphenoxy group, naphthoxy group, biphenyloxy group, and the like. As amino groups, there can be mentioned are dimethylamino group, diethylamino group, dibutylamino group,



dioctylamino group, N-methyl-N-hexylamino group, dicyclohexylamino group, diphenylamino group, N-methyl-N-phenylamino, and the like.

[0098]

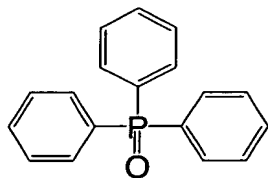
Preferred as  $R^{21}$  to  $R^{23}$  are an alkyl group, an aryl group, an alkoxy group, and an aryloxy group. Concerning the effect of the invention, it is preferred that at least one or more of  $R^{21}$  to  $R^{23}$  are an alkyl group or an aryl group, and more preferably, two or more of them are an alkyl group or an aryl group. From the viewpoint of low cost availability, it is preferred that  $R^{21}$  to  $R^{23}$  are of the same group.

Specific examples of hydrogen bonding compounds represented by general formula (D) of the invention and others are shown below, but it should be understood that the invention is not limited thereto.

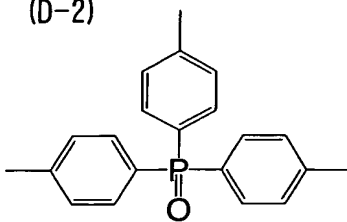
[0099]

[Formula 8]

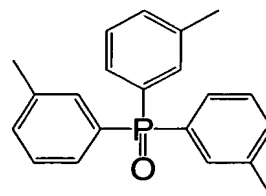
(D-1)



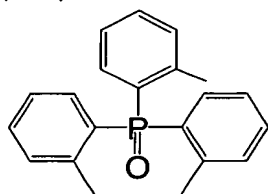
(D-2)



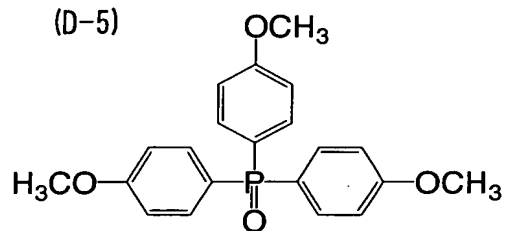
(D-3)



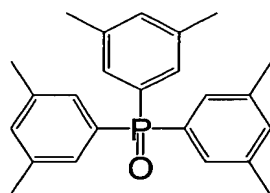
(D-4)



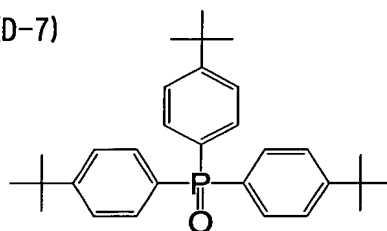
(D-5)



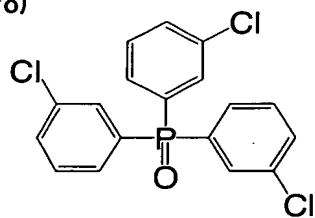
(D-6)



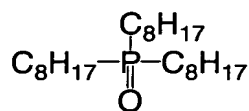
(D-7)



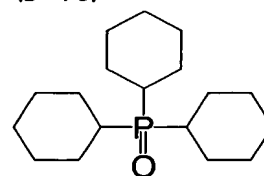
(D-8)



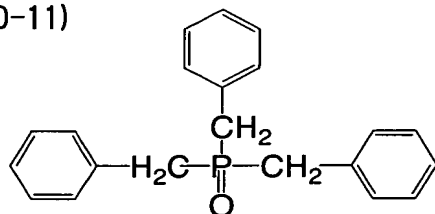
(D-9)



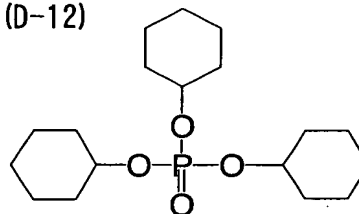
(D-10)



(D-11)

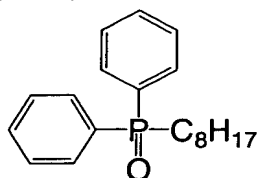


(D-12)

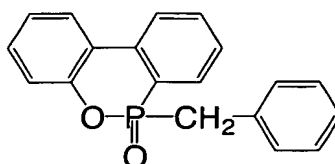


[0100]  
[Formula 9]

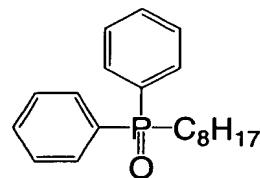
(D-13)



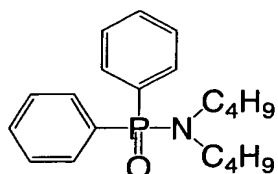
(D-14)



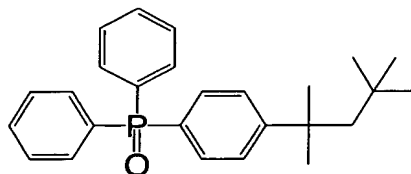
(D-15)



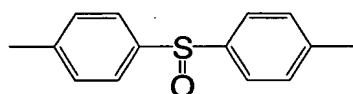
(D-16)



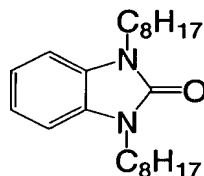
(D-17)



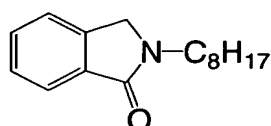
(D-18)



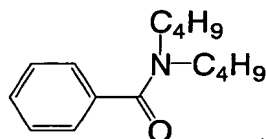
(D-19)



(D-20)



(D-21)



[0101]

Specific examples of hydrogen bonding compounds other than those enumerated above can be found in those described in EP-A No. 1096310 and in Japanese Patent Application Nos. 2000-270498 and 2001-124796.

The compound expressed by general formula (D) used in the invention can be used in the photosensitive material by being incorporated into the coating solution in the form of solution, emulsion dispersion, or solid-dispersed fine particle dispersion similar to the case of reducing agent, however, it is preferred to be used after it is prepared in the form of solution. In the solution, the compound expressed by general formula (D) forms a hydrogen-bonded complex with a compound having a phenolic hydroxyl group, and can be isolated as a complex in crystalline state depending on the combination of the reducing agent and the compound expressed by general formula (D). It is particularly preferred to use the crystal powder thus isolated in the form of a solution by dissolving it into a coating solvent, because it provides stable performance.

The compound expressed by general formula (D) is preferably used in a range of from 1 to 200 mol%, more preferably from 10 to 150 mol%, and most preferably, from 20 to

100 mol%, with respect to the reducing agent.

[0102]

#### 8. Binder

Any type of polymer may be used as the binder for the image forming layer in the photosensitive material of the invention. Suitable as the binder are those that are transparent or translucent, and that are generally colorless, such as natural resin or polymer and their copolymers; synthetic resin or polymer and their copolymers; or media forming a film; for example, included are gelatin, rubber, poly(vinyl alcohol), hydroxyethyl cellulose, cellulose acetate, cellulose acetate butyrate, poly(vinyl pyrrolidone), casein, starch, poly(acrylic acid), poly(methylmethacrylic acid), poly(vinyl chloride), poly(methacrylic acid), styrene-maleic anhydride copolymers, styrene-acrylonitrile copolymers, styrene-butadiene copolymers, poly(vinyl acetal) (e.g., poly(vinyl formal) and poly(vinyl butyral)), poly(ester), poly(urethane), phenoxy resin, poly(vinylidene chloride), poly(epoxide), poly(carbonate), poly(vinyl acetate), poly(olefin), cellulose esters, and poly(amide).

[0103]

If necessary, two or more binders may be used. In such a case, two or more types of polymers differing in glass transition temperature (which is denoted as  $T_g$  hereinafter) may be blended for use.

[0104]

In the specification,  $T_g$  was calculated according to the following equation.

$$1/T_g = \Sigma(X_i/T_{gi})$$

Where, the polymer is obtained by copolymerization of  $n$  monomer compounds (from  $i=1$  to  $i=n$ );  $X_i$  represents the mass fraction of the  $i$ th monomer ( $\Sigma X_i=1$ ), and  $T_{gi}$  is the glass transition temperature (absolute temperature) of the homopolymer obtained with the  $i$ th monomer. The symbol  $\Sigma$  stands for the summation from  $i=1$  to  $i=n$ . Values for the glass transition temperature ( $T_{gi}$ ) of the homopolymers derived from each of the monomers were obtained from J. Brandrup and E.H. Immergut, Polymer Handbook (3rd Edition)(Wiley-Interscience, 1989).

[0105]

#### 1) Binder for organic solvents

In the case the binder is applied by using the following organic solvents, any of those below can be selected: polyvinyl acetal, polyvinyl chloride, polyvinyl acetate, cellulose acetate, polyolefin, polyester, polystyrene, polyacrylonitrile, polycarbonate, polyvinyl butyral, butylethyl cellulose, metacrylate copolymer, maleic anhydride ester copolymers, polystyrene and butadiene-styrene copolymers, and the like. In the image forming layer, in particular, polyvinyl butyral is preferably incorporated as the binder. More specifically, polyvinyl butyral is added as a binder to account for 50% by mass or more with respect to the total composition of the binder for the image forming layer. As a matter of fact, copolymers and terpolymers are also included. The preferred total content of polyvinyl butyral is in a range of 50% by mass to 100% by mass, more preferably, is in a range of 70% by mass to 100% by mass, with respect to the total composition of the binder incorporated in the image forming layer. The  $T_g$  of the binder is preferably in a range of from 40 to 90 °C, and more preferably, from 50 to 80 °C. In the case two or more types of polymers differing in  $T_g$  are used as a blend, the weight average  $T_g$  preferably falls in the above range.

[0106]

The total amount of the binders is such that, for instance, the components of the image forming layer can be sufficiently maintained within the layer. That is, the binders are used in an amount effective to function as binder. The effective range can be properly determined by those skilled in the art. In the case of holding at least an organic silver salt, the suitable mass ratio of the binders to the organic silver salt is from 15:1 to 1:3, particularly preferably, from 8:1 to 1:2.

Specific examples of solvents can be found in Solvent Pocket Book (new edition) (Ohm Publishing, 1994), but the invention is not limited thereto. Furthermore, the boiling point of the solvents used in the invention is preferably in a range of 40°C to 180 °C. As examples of the solvents, specifically mentioned are hexane, cyclohexane, toluene, methanol, ethanol, isopropanol, acetone, methyl ethyl ketone, ethyl acetate, 1,1,1-trichloroethane, tetrahydrofuran, triethylamine, thiophene, trifluoroethanol, perfluoropentane, xylene, n-butanol, phenol, methyl isobutyl ketone, cyclohexanone, butyl acetate, diethyl carbonate, chlorobenzene, dibutyl ether, anisole, ethylene glycol diethyl ether, N,N-dimethylformamide, morpholine, propanesultone, perfluorotributylamine, water, and the like. Among them, methyl ethyl ketone is preferably used, because it has a favorable boiling point and is capable of providing a uniform coated film plane with less load of drying and with less solvent residues.

[0107]

After coating and drying, it is preferred that the solvent used for the coating remains less in the film. In general, residual solvent volatilizes into the environment on exposing or thermal developing the photothermographic material, which not only makes people uncomfortable but also is harmful to the health.

[0108]

In the case of using MEK in the invention, the residual amount of MEK is preferably in a range of from 0.1 mg/m<sup>2</sup> to 150 mg/m<sup>2</sup>, more preferably, from 0.1 mg/m<sup>2</sup> to 80 mg/m<sup>2</sup>, and most preferably, from 0.1 mg/m<sup>2</sup> to 40 mg/m<sup>2</sup>.

[0109]

## 2) Binder for water solvent

In the case the layer containing organic silver salt is formed by first applying a coating solution containing 30% by mass or more of water in the solvent and by then drying, and furthermore, in the case the binder of the layer containing organic silver salt is soluble or dispersible in an aqueous solvent (water solvent), the performance can be ameliorated particularly in the case a polymer latex having an equilibrium water content of 2% by mass or lower at 25°C and 60%RH is used. Most preferred embodiment is such prepared to yield an ion conductivity of 2.5 mS/cm or lower, and as such a preparation method, there can be mentioned a refining treatment using a separation function membrane after synthesizing the polymer.

[0110]

The aqueous solvent in which the polymer is soluble or dispersible, as referred to herein, signifies water or water containing 70 % by mass or less of a water-admixing organic solvent mixed therein. As water-admixing organic solvents, there can be mentioned, for example, alcohols such as methyl alcohol, ethyl alcohol, propyl alcohol, and the like; cellosolves such as methyl cellosolve, ethyl cellosolve, butyl cellosolve, and the like; ethyl acetate, dimethylformamide, and the like.

[0111]

The term “aqueous solvent” is also used in the case the polymer is not thermodynamically dissolved, but is present in a so-called dispersed state.

[0112]

The term “equilibrium water content at 25°C and 60%RH” as referred to herein can be expressed as follows:

Equilibrium water content at 25°C and 60%RH

$$= [(W1 - W0)/W0] \times 100 (\% \text{ by mass})$$

where, W1 is the weight of the polymer in moisture-controlled equilibrium under the atmosphere of 25°C and 60%RH, and W0 is the absolutely dried weight of the polymer at 25°C.

[0113]

For the definition and the method of measurement for water content, reference can be made to Polymer Engineering Series 14, “Testing methods for polymeric materials” (The Society of Polymer Science, Japan, published by Chijin Shokan).

[0114]

The equilibrium water content at 25°C and 60%RH is preferably 2% by mass or lower, but is more preferably, 0.01% by mass to 1.5% by mass, and is most preferably, 0.02% by mass to 1% by mass.

[0115]

Examples of dispersed states may include a latex, in which water-insoluble fine particles of hydrophobic polymer are dispersed, or such in which polymer molecules are dispersed in molecular states or by forming micelles, but preferred are latex-dispersed particles. The average particle size of the dispersed particles is in a range of from 1 to 50,000 nm, preferably 5 nm to 1,000 nm, more preferably, 10 nm to 500 nm, and most preferably, 50 nm to 200 nm. There is no particular limitations concerning particle size distribution of the dispersed particles, and the dispersed particles may be widely distributed or may exhibit a monodisperse particle size distribution. From the viewpoint of controlling the physical properties of the coating solution, preferred mode of usage includes mixing two or more types of particles each having monodisperse particle distribution.

[0116]

In the invention, preferred embodiment of the polymers capable of being dispersed in an aqueous solvent includes hydrophobic polymers such as acrylic polymers, poly(ester), rubber (e.g., SBR resin), poly(urethane), poly(vinyl chloride), poly(vinyl acetate), poly(vinylidene chloride), poly(olefin), and the like. As the polymers above, usable are straight chain polymers, branched polymers, or crosslinked polymers; also usable are so-called homopolymers in which single monomer is polymerized, or copolymers in which two or more types of monomers are polymerized. In the case of a copolymer, it may be a random copolymer or a block copolymer. The molecular weight of these polymers is, in number average molecular weight, in a range of from 5,000 to 1,000,000, preferably from 10,000 to 200,000. Those having too small molecular weight exhibit insufficient mechanical strength on forming the image forming layer, and those having too large molecular weight are also not preferred because the filming properties are poor. Further, crosslinking polymer latexes are particularly preferred for use.

[0117]

Specific examples of preferred polymer latexes are given below, which are expressed by the starting monomers with % by mass given in parenthesis. The molecular weight is given in number average molecular weight. In the case a polyfunctional monomer is used, the concept of molecular weight is not applicable because they build a crosslinked structure. Hence, they are denoted as "crosslinking", and the molecular weight is omitted. Tg represents glass transition temperature.

[0118]

- P-1; Latex of -MMA(70)-EA(27)-MAA(3)- (molecular weight 37000, Tg 61°C)  
P-2; Latex of -MMA(70)-2EHA(20)-St(5)-AA(5)- (molecular weight 40000, Tg 59°C)  
P-3; Latex of -St(50)-Bu(47)-MAA(3)- (crosslinking, Tg -17°C)  
P-4; Latex of -St(68)-Bu(29)-AA(3)- (crosslinking, Tg 17°C)  
P-5; Latex of -St(71)-Bu(26)-AA(3)- (crosslinking, Tg 24°C)  
P-6; Latex of -St(70)-Bu(27)-IA(3)- (crosslinking)  
P-7; Latex of -St(75)-Bu(24)-AA(1)- (crosslinking, Tg 29°C)  
P-8; Latex of -St(60)-Bu(35)-DVB(3)-MAA(2)- (crosslinking)  
P-9; Latex of -St(70)-Bu(25)-DVB(2)-AA(3)- (crosslinking)  
P-10; Latex of -VC(50)-MMA(20)-EA(20)-AN(5)-AA(5)- (molecular weight 80000)  
P-11; Latex of -VDC(85)-MMA(5)-EA(5)-MAA(5)- (molecular weight 67000)  
P-12; Latex of -Et(90)-MAA(10)- (molecular weight 12000)  
P-13; Latex of -St(70)-2EHA(27)-AA(3)- (molecular weight 130000, Tg 43°C)  
P-14; Latex of -MMA(63)-EA(35)-AA(2)- (molecular weight 33000, Tg 47°C)  
P-15; Latex of -St(70.5)-Bu(26.5)-AA(3)- (crosslinking, Tg 23°C)  
P-16; Latex of -St(69.5)-Bu(27.5)-AA(3)- (crosslinking, Tg 20.5°C)

[0119]

In the structures above, abbreviations represent monomers as follows. MMA: methyl metacrylate, EA: ethyl acrylate, MAA: methacrylic acid, 2EHA: 2-ethylhexyl acrylate, St: styrene, Bu: butadiene, AA: acrylic acid, DVB: divinylbenzene, VC: vinyl chloride, AN: acrylonitrile, VDC: vinylidene chloride, Et: ethylene, IA: itaconic acid.

[0120]

The polymer latexes above are commercially available, and polymers below are usable. As examples of acrylic polymers, there can be mentioned Cevian A-4635, 4718, and 4601 (all manufactured by Daicel Chemical Industries, Ltd.), Nipol Lx811, 814, 821, 820, and 857 (all manufactured by Nippon Zeon Co., Ltd.), and the like; as examples of poly(ester), there can be mentioned FINETEX ES650, 611, 675, and 850 (all manufactured by Dainippon Ink and Chemicals, Inc.), WD-size and WMS (all manufactured by Eastman Chemical Co.), and the like; as examples of poly(urethane), there can be mentioned HYDRAN AP10, 20, 30, and 40 (all manufactured by Dainippon Ink and Chemicals, Inc.), and the like; as examples of rubber, there can be mentioned LACSTAR 7310K, 3307B, 4700H, and 7132C (all manufactured by Dainippon Ink and Chemicals, Inc.), Nipol Lx416, 410, 438C, and 2507 (all manufactured by Nippon Zeon Co., Ltd.), and the like; as examples of poly(vinyl chloride), there can be mentioned G351 and G576 (all manufactured by Nippon Zeon Co., Ltd.), and the like; as examples of poly(vinylidene chloride), there can be mentioned L502 and L513 (all manufactured by Asahi Chemical Industry Co., Ltd.), and the like; as examples of poly(olefin), there can be mentioned Chemipearl S120 and SA100 (all manufactured by

Mitsui Petrochemical Industries, Ltd.), and the like.

[0121]

The polymer latexes above may be used alone, or may be used by blending two or more types depending on needs.

[0122]

Particularly preferred as the polymer latex for use in the invention is that of styrene-butadiene copolymer. The weight ratio of monomer unit for styrene to that of butadiene constituting the styrene-butadiene copolymer is preferably in a range of from 40:60 to 95:5. Further, the monomer unit of styrene and that of butadiene preferably accounts for 60 to 99% by mass with respect to the copolymer. Moreover, the polymer latex of the invention contains acrylic acid or methacrylic acid, preferably, for 1 to 6% by mass, and more preferably, for 2 to 5% by mass, with respect to the total mass of the monomer unit of styrene and that of butadiene. The polymer latex of the invention preferably contains acrylic acid. The preferred range of the molecular weight is the same as that described above.

[0123]

As the latex of styrene-butadiene copolymer preferably used in the invention, there can be mentioned P-3 to P-8 and P-15, or commercially available LACSTAR-3307B, 7132C, Nipol Lx416, and the like.

[0124]

In the layer containing organic silver salt of the photosensitive material according to the invention, if necessary, there can be added hydrophilic polymers such as gelatin, polyvinyl alcohol, methyl cellulose, hydroxypropyl cellulose, carboxymethyl cellulose, and the like. The hydrophilic polymers above are added in an amount of 30% by mass or less, preferably 20% by mass or less, with respect to the total weight of the binder incorporated in the layer containing organic silver salt.

[0125]

The layer containing organic silver salt is, in general, a photosensitive layer (emulsion layer) containing a photosensitive silver halide, i.e., the photosensitive silver salt; in such a case, the weight ratio of total binder to silver halide is in a range of from 400 to 5, more preferably, from 200 to 10.

[0126]

In the case water solvent is used for the preparation, the total binder content in the image forming layer is preferably in a range of from 0.2 g/m<sup>2</sup> to 30 g/m<sup>2</sup>, more preferably from 1 g/m<sup>2</sup> to 15 g/m<sup>2</sup>, and most preferably, from 2 g/m<sup>2</sup> to 10 g/m<sup>2</sup>. In the image forming layer of the invention, there may be added a crosslinking agent for crosslinking, or a surface active agent and the like to improve coating properties.

[0127]

#### 10. Surface active agent

As the surface active agent, the solvent, the support, antistatic agent or the electrically conductive layer, and the method for obtaining color images applicable in the invention, there can be mentioned those disclosed in paragraph Nos. 0132, 0133, 0134, 0135, and 0136, respectively, of JP-A No. 11-65021. The lubricant is described in paragraph Nos. 0061 to 0064 of JP-A No. 11-84573 and in paragraph Nos. 0049 to 0062 of Japanese Patent



Application No. 11-106881.

In the invention, preferably used is a fluorocarbon surface active agent. Specific examples of fluorocarbon surface active agents can be found in those described in JP-A Nos. 10-197985, 2000-19680, and 2000-214554. Polymer fluorocarbon surface active agents described in JP-A 9-281636 can be also used preferably. For the photothermographic material in the invention, the fluorocarbon surface active agents described in JP-A Nos. 2002-82411, 2001-242357, and 2001-264110 are preferably used. Especially, the use of the fluorocarbon surface active agents described in JP-A Nos. 2001-242357 and 2001-264110 in an aqueous coating solution is preferred from the standpoint of capacity in static control, stability of the coating side state and sliding facility. The fluorocarbon surface active agent described in JP-A No. 2001-264110 is mostly preferred because of high capacity in static control and that it needs small amount to use.

According to the invention, the fluorocarbon surface active agent can be used on either image forming layer side or back layer side, but is preferred to use on the both sides. Further, it is particularly preferred to use the fluorocarbon surface active agent in combination with an electrically conductive layer including aforementioned metal oxides. In this case, the amount of the fluorocarbon surface active agent on the side of the electrically conductive layer can be reduced or removed.

The amount of the fluorocarbon surface active agent used is preferably in the range of 0.1 mg/m<sup>2</sup> to 100 mg/m<sup>2</sup> on each side of image forming layer and back layer, more preferably 0.3 mg/m<sup>2</sup> to 30 mg/m<sup>2</sup>, further preferably 1 mg/m<sup>2</sup> to 10 mg/m<sup>2</sup>. Especially, the fluorocarbon surface active agent described in JP-A No. 2001-264110 is effective, and is used preferably in the range of 0.01 mg/m<sup>2</sup> to 10 mg/m<sup>2</sup>, more preferably 0.01 mg/m<sup>2</sup> to 5 mg/m<sup>2</sup>.

[0128]

#### 11. Toner

In the photothermographic material of the present invention, the addition of a toner is preferred. The description of the toner can be found in JP-A No. 10-62899 (paragraph Nos. 0054 to 0055), EP-A No. 0803764A1 (page21, lines 23 to 48), JP-A Nos. 2000-356317 and 2000-187298. Particularly preferred are phthalazinones (phthalazinone, phthalazinone derivatives and metal salts thereof, e.g., 4-(1-naphthyl)phthalazinone, 6-chlorophthalazinone, 5,7-dimethoxyphthalazinone and 2,3-dihydro-1,4-phthalazinedione); combinations of phthalazinones and phthalic acids(e.g., phthalic acid, 4-methylphthalic acid, 4-nitrophthalic acid, diammonium phthalate, sodium phthalate, potassium phthalate and tetrachlorophthalic anhydride); phthalazines(phthalazine, phthalazine derivatives and metal salts thereof, e.g., 4-(1-naphthyl)phthalazine, 6-isopropylphthalazine, 6-ter-butylphthalazine, 6-chlorophthalazine, 5,7-dimethoxyphthalazine and 2,3-dihydrophthalazine). In the iodide rich silver halide, particularly preferred is a combination of phthalazines and phthalic acids.

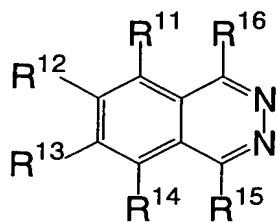
[0129]

In the present invention, a high speed transportation process and a developing apparatus in which the distance between the exposing section and the developing section is short are used. For these reasons, there is a possibility that phtalazines cause a contaminant as volatiles and contaminate the exposing section, the developing section and phothothermographic material itself. To prevent this contamination, it is preferred to use the phtalazines represented by the following general formula (I).

[0130]

[Formula 10]

# General Formula (I)



[0131]

$R^{11}$ ,  $R^{12}$ ,  $R^{13}$ ,  $R^{14}$ ,  $R^{15}$  and  $R^{16}$  each independently represent a hydrogen atom or monovalent substituent which may combine each other to form a ring. But, all of  $R^{11}$ ,  $R^{12}$ ,  $R^{13}$ ,  $R^{14}$ ,  $R^{15}$  and  $R^{16}$  can not be hydrogen atoms. Examples of substituents are an alkyl group (preferably an alkyl group having 1 to 20 carbon atoms, more preferably an alkyl group having 1 to 12 carbon atoms, most preferably an alkyl group having 1 to 8 carbon atoms; e.g., a methyl group, an ethyl group, a n-propyl group, an iso-propyl group, a n-butyl group, a sec-butyl group, an iso-butyl group, a tert-butyl group, a n-pentyl group, a tert-pentyl group, a n-hexyl group, a n-octyl group, a n-decyl group, a n-hexadecyl group, a cyclopropyl group, a cyclopentyl group, a cyclohexyl group, a benzyl group and so on), an alkenyl group, (preferably an alkenyl group having 2 to 20 carbon atoms, more preferably an alkenyl group having 2 to 12 carbon atoms, most preferably an alkenyl group having 2 to 8 carbon atoms; e.g., a vinyl group, an allyl group, a 2-butenyl group, a 3-pentenyl group and so on), an alkynyl group (preferably an alkynyl group having 2 to 20 carbon atoms, more preferably an alkynyl group having 2 to 12 carbon atoms, most preferably an alkynyl group having 2 to 8 carbon atoms; e.g., a propargyl group, a 3-pentynyl group and so on), an aryl group (preferably an aryl group having 6 to 30 carbon atoms, more preferably an aryl group having 6 to 20 carbon atoms, most preferably an aryl group having 6 to 12 carbon atoms; e.g., a phenyl group, a p-methylphenyl group, a naphthyl group and so on), an amino group (preferably an amino group having 0 to 20 carbon atoms, more preferably an amino group having 0 to 10 carbon atoms, most preferably an amino group having 0 to 6 carbon atoms; e.g., an amino group, a methylamino group, a dimethylamino group, a diethylamino group, a dibenzylamino group and so on), an alkoxy group (preferably an alkoxy group having 1 to 20 carbon atoms, more preferably an alkoxy group having 1 to 12 carbon atoms, most preferably an alkoxy group having 1 to 8 carbon atoms; e.g., a methoxy group, an ethoxy group, an isopropoxy group, a butoxy group and so on), an aryloxy group (preferably an aryloxy group having 6 to 20 carbon atoms, more preferably an aryloxy group having 6 to 16 carbon atoms, most preferably an aryloxy group having 6 to 12 carbon atoms; e.g., a phenyloxy group, a 2-naphthyloxy group and so on), an acyl group (preferably an acyl group having 1 to 20 carbon atoms, more preferably an acyl group having 1 to 16 carbon atoms, most preferably an acyl group having 1 to 12 carbon atoms; e.g., an acetyl group, a benzoyl group, a formyl group, a pivaloyl group and so on), an alkoxycarbonyl group (preferably an alkoxycarbonyl group having 2 to 20 carbon atoms, more preferably an alkoxycarbonyl group having 2 to 16 carbon atoms, most preferably an alkoxycarbonyl group having 2 to 12 carbon atoms; e.g., a methoxycarbonyl group, an ethoxycarbonyl group and so on), an aryloxycarbonyl group (preferably an aryloxycarbonyl group having 7 to 20 carbon atoms, more preferably an aryloxycarbonyl group having 7 to 16 carbon atoms, most preferably an aryloxycarbonyl group having 7 to 10 carbon atoms; e.g., a phenyloxycarbonyl group and so on), an acyloxy group (preferably an acyloxy group having 2 to 20 carbon atoms, more preferably an acyloxy

group having 2 to 16 carbon atoms, most preferably an acyloxy group having 2 to 12 carbon atoms; e.g., an acetoxy group, a benzoyloxy group and so on), an acylamino group (preferably an acylamino group having 2 to 20 carbon atoms, more preferably an acylamino group having 2 to 16 carbon atoms, most preferably an acylamino group having 2 to 10 carbon atoms; e.g., an acetylamino group, a benzoylamino group and so on), an alkoxycarbonylamino group (preferably an alkoxycarbonylamino group having 2 to 20 carbon atoms, more preferably an alkoxycarbonylamino group having 2 to 16 carbon atoms, most preferably an alkoxycarbonylamino group having 2 to 12 carbon atoms; e.g., a methoxycarbonylamino group and so on), an aryloxycarbonylamino group (preferably an aryloxycarbonylamino group having 7 to 20 carbon atoms, more preferably an aryloxycarbonylamino group having 7 to 16 carbon atoms, most preferably an aryloxycarbonylamino group having 7 to 12 carbon atoms; e.g., a phenyloxycarbonylamino group and so on), a sulfonylamino group (preferably a sulfonylamino group having 1 to 20 carbon atoms, more preferably a sulfonylamino group having 1 to 16 carbon atoms, most preferably a sulfonylamino group having 1 to 12 carbon atoms; e.g., a methanesulfonylamino group, a benzenesulfonylamino group and so on), a sulfamoyl group (preferably a sulfamoyl group having 0 to 20 carbon atoms, more preferably a sulfamoyl group having 0 to 16 carbon atoms, most preferably a sulfamoyl group having 0 to 12 carbon atoms; e.g., a sulfamoyl group, a methylsulfamoyl group, a dimethylsulfamoyl group, a phenylsulfamoyl group and so on), a carbamoyl group (preferably a carbamoyl group having 1 to 20 carbon atoms, more preferably a carbamoyl group having 1 to 16 carbon atoms, most preferably a carbamoyl group having 1 to 12 carbon atoms; e.g., a carbamoyl group, a methylcarbamoyl group, a diethylcarbamoyl group, a phenylcarbamoyl group and so on), an alkylthio group (preferably an alkylthio group having 1 to 20 carbon atoms, more preferably an alkylthio group having 1 to 16 carbon atoms, most preferably an alkylthio group having 1 to 12 carbon atoms; e.g., a methylthio group, an ethylthio group and so on), an arylthio group (preferably an arylthio group having 6 to 20 carbon atoms, more preferably an arylthio group having 6 to 16 carbon atoms, most preferably an arylthio group having 6 to 12 carbon atoms; e.g., a phenylthio group and so on), a sulfonyl group (preferably a sulfonyl group having 1 to 20 carbon atoms, more preferably a sulfonyl group having 1 to 16 carbon atoms, most preferably a sulfonyl group having 1 to 12 carbon atoms; e.g., a mesyl group, a tosyl group and so on), a sulfinyl group (preferably a sulfinyl group having 1 to 20 carbon atoms, more preferably a sulfinyl group having 1 to 16 carbon atoms, most preferably a sulfinyl group having 1 to 12 carbon atoms; e.g., a methanesulfinyl group, a benzenesulfinyl group and so on), an ureido group (preferably an ureido group having 1 to 20 carbon atoms, more preferably an ureido group having 1 to 16 carbon atoms, most preferably an ureido group having 1 to 12 carbon atoms; e.g., an ureido group, a methylureido group, a phenylureido group and so on), a phosphoramido group (preferably a phosphoramido group having 1 to 20 carbon atoms, more preferably a phosphoramido group having 1 to 16 carbon atoms, most preferably a phosphoramido group having 1 to 12 carbon atoms; e.g., a diethylphosphoramido group, a phenylphosphoramido group and so on), a hydroxy group, a mercapto group, a halogen atom (e.g., a fluorine atom, a chlorine atom, a bromine atom and an iodine atom), a cyano group, a sulfo group, a carboxyl group, a nitro group, a hydroxamic acid group, a sulfino group, a hydrazino group and a hetero ring group (e.g., an imidazolyl group, a pyridyl group, a furyl group, a piperidyl group, a morpholino group, a thienyl group and so on) and so on. These substituents can further be substituted by another substituents, and the substituents capable of forming salt can form a salt thereof. Examples of the ring formed by binding of R<sup>11</sup> to R<sup>16</sup> include a dioxolene ring and a benzene ring and so on.

[0132]

In the present invention, preferred substituents of R<sup>11</sup>, R<sup>12</sup>, R<sup>13</sup> and R<sup>14</sup> in general

formula (I) are a hydrogen atom, an alkyl group, an aryl group, a halogen atom and an acyl group. More preferred substituents are a hydrogen atom, an alkyl group, an aryl group and an acyl group and particularly preferred compounds are a hydrogen atom and an alkyl group. For  $R^{15}$  and  $R^{16}$ , a hydrogen atom is preferred.

[0133]

Examples represented by general formula (I) of the present invention can be prepared easily by those skilled in the art by using the known method described in R. G. Elderfield, "Heterocyclic Compounds", John Wiley and Sons, Vol. 1-9 (1950-1967) or A.R. Katritzky, "Comprehensive Heterocyclic Chemistry", Pergamon Press (1984), and so on.

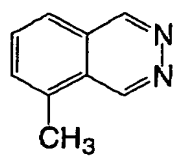
[0134]

Specific examples of general formula (I) of the present invention are set forth below, however, the present invention is not limited to these specific examples.

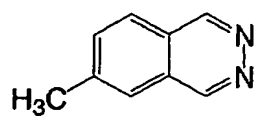
[0135]

[Formula 11]

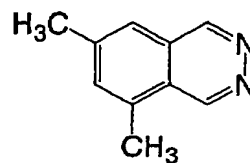
(1-1)



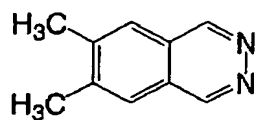
(1-2)



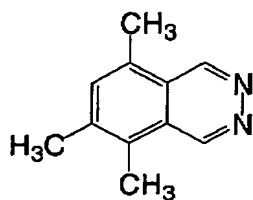
(1-3)



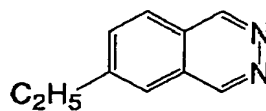
(1-4)



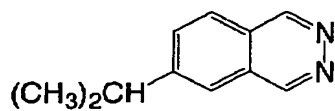
(1-5)



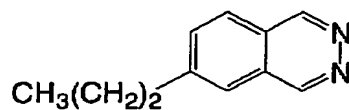
(1-6)



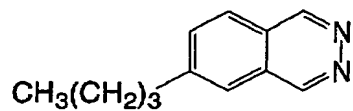
(1-7)



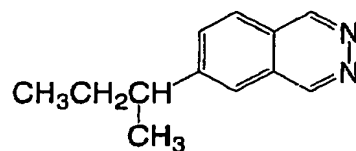
(1-8)



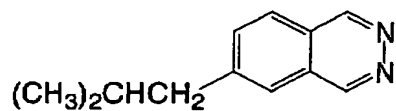
(1-9)



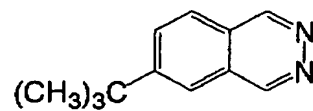
(1-10)



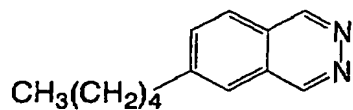
(1-11)



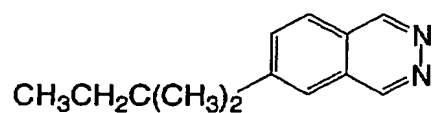
(1-12)



(1-13)

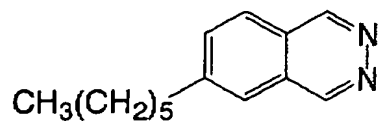


(1-14)

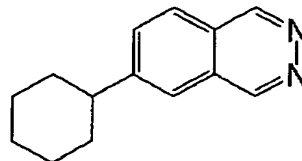


[0136]  
[Formula 12]

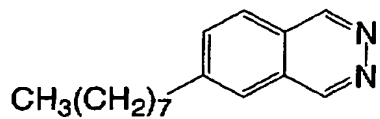
(1-15)



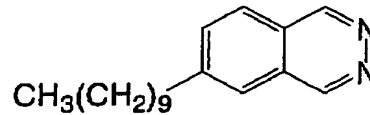
(1-16)



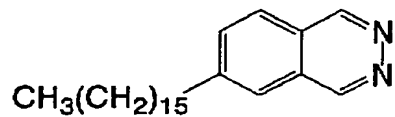
(1-17)



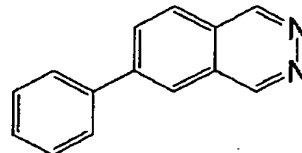
(1-18)



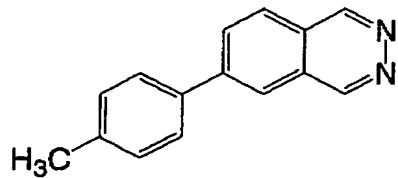
(1-19)



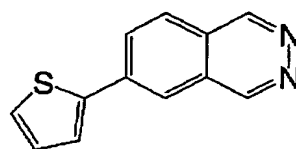
(1-20)



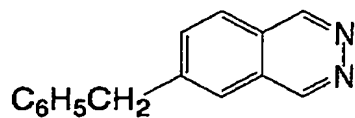
(1-21)



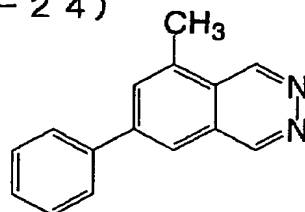
(1-22)



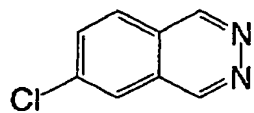
(1-23)



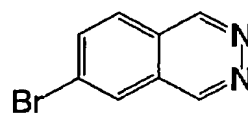
(1-24)



(1-25)



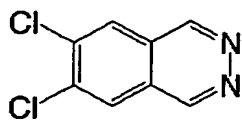
(1-26)



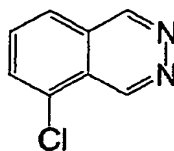
[0137]

[Formula 13]

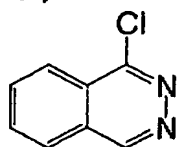
(1-27)



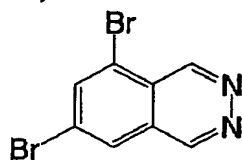
(1-28)



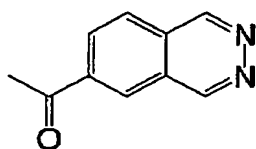
(1-29)



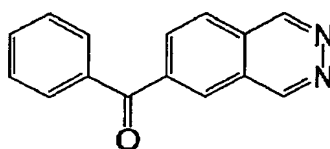
(1-30)



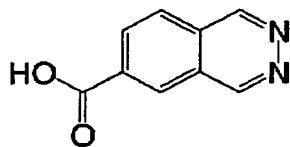
(1-31)



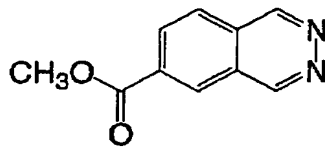
(1-32)



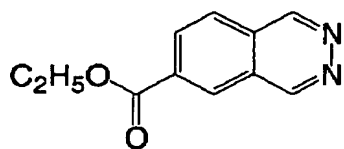
(1-33)



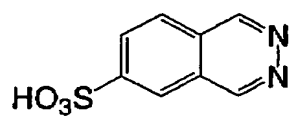
(1-34)



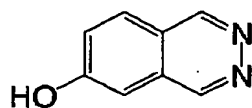
(1-35)



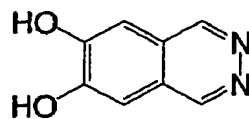
(1-36)



(1-37)



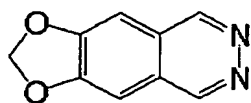
(1-38)



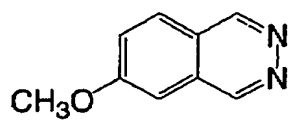
[0138]

[Formula 14]

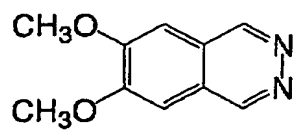
(1-39)



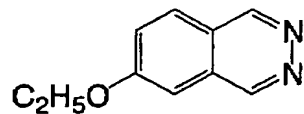
(1-40)



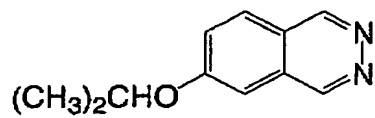
(1-41)



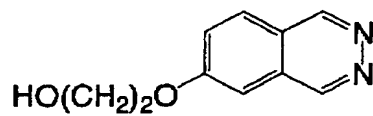
(1-42)



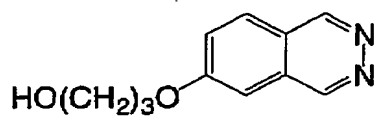
(1-43)



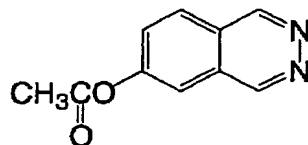
(1-44)



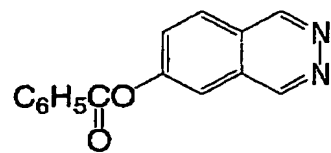
(1-45)



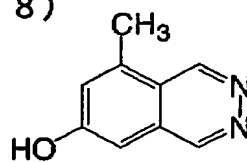
(1-46)



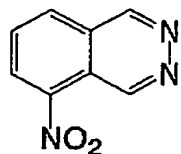
(1-47)



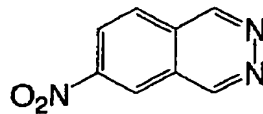
(1-48)



(1-49)



(1-50)

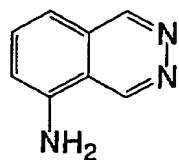




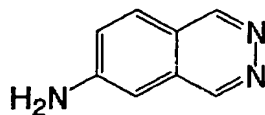
[0139]

[Formula 15]

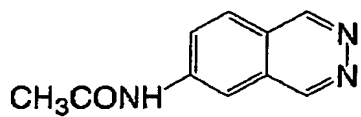
( 1 - 5 1 )



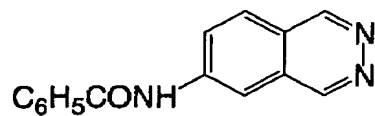
( 1 - 5 2 )



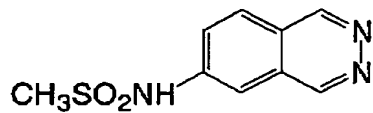
( 1 - 5 3 )



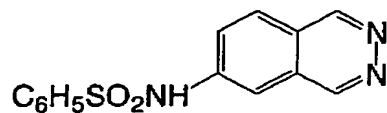
( 1 - 5 4 )



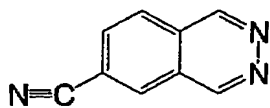
( 1 - 5 5 )



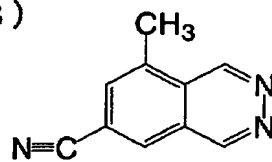
( 1 - 5 6 )



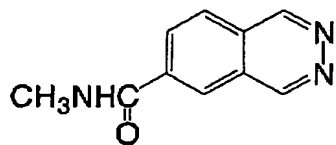
( 1 - 5 7 )



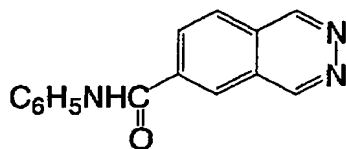
( 1 - 5 8 )



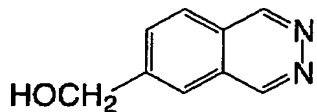
( 1 - 5 9 )



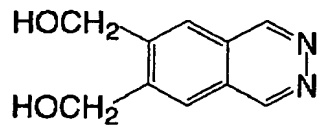
( 1 - 6 0 )



( 1 - 6 1 )



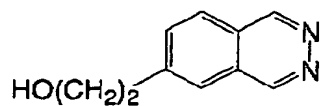
( 1 - 6 2 )



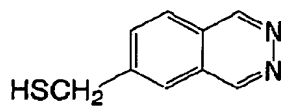
[0140]

[Formula 16]

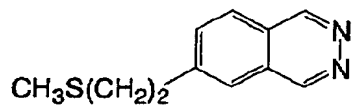
(1-63)



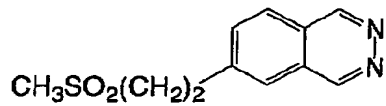
(1-64)



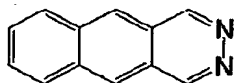
(1-65)



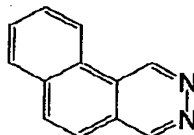
(1-66)



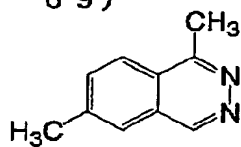
(1-67)



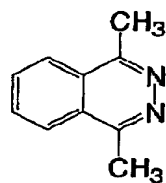
(1-68)



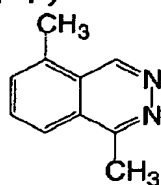
(1-69)



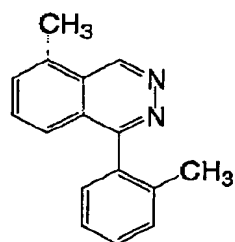
(1-70)



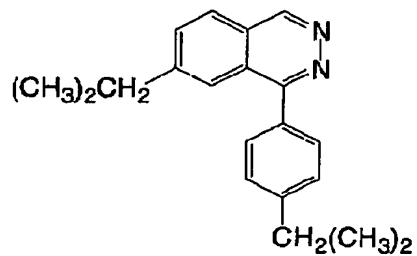
(1-71)



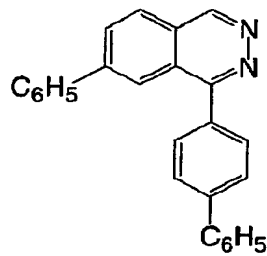
(1-72)



(1-73)

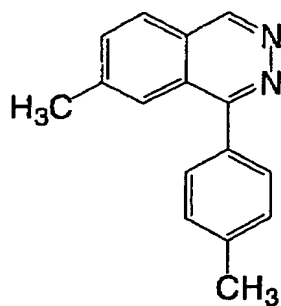


(1-74)

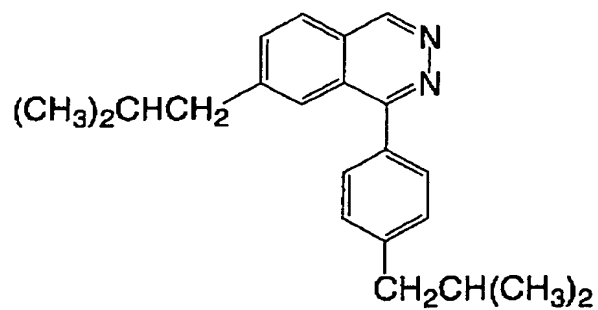


[0141]  
[Formula 17]

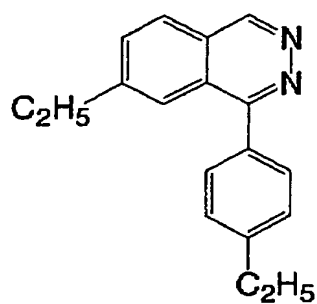
(1-75)



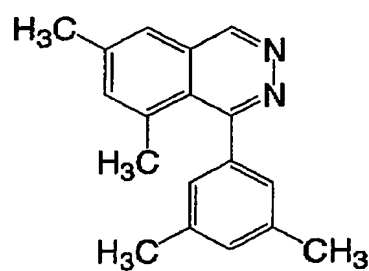
(1-76)



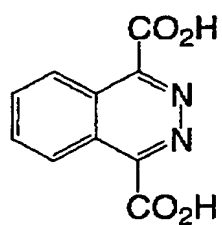
(1-77)



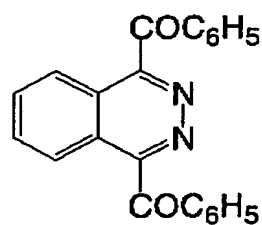
(1-78)



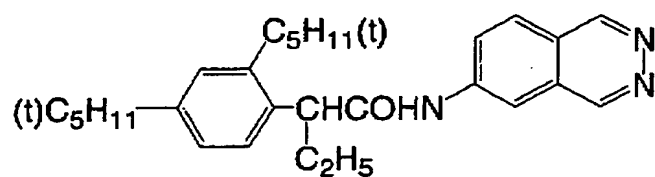
(1-79)



(1-80)

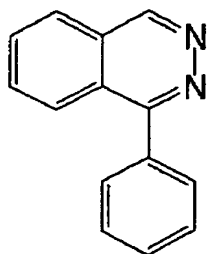


(1-81)

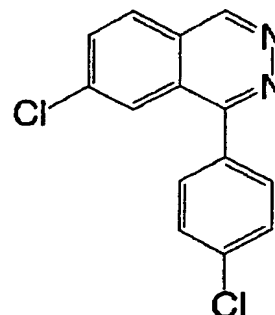


[0142]  
[Formula 18]

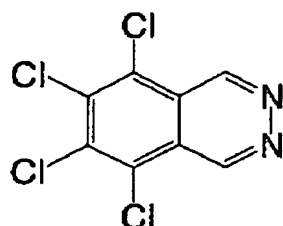
( 1 - 8 2 )



( 1 - 8 3 )



( 1 - 8 4 )



[0143]

12. Other additives

In the invention, mercapto compounds, disulfide compounds, and thione compounds may be added in order to control the development by suppressing or enhancing development, to improve spectral sensitization efficiency, or to improve storage properties before and after development. Descriptions can be found in paragraph Nos. 0067 to 0069 of JP-A No. 10-62899, a compound expressed by general formula (I) of JP-A No. 10-186572 and specific examples thereof shown in paragraph Nos. 0033 to 0052, and in lines 36 to 56 in page 20 of EP No. 0803764A1. Among them, mercapto-substituted heterocyclic aromatic compounds described in JP-A Nos. 9-297367, 9-304875, and 2001-100358, as well as in Japanese Patent Application Nos. 2001-104213 and 2001-104214, and the like, are particularly preferred.

[0144]

Plasticizers and lubricants usable in the photothermographic material of the invention are described in paragraph No. 0117 of JP-A No. 11-65021. Lubricants are described in paragraph Nos. 0061 to 0064 of JP-A No. 11-84573 and in paragraph Nos. 0049 to 0062 of Japanese Patent Application No. 11-106881.

[0145]

From the viewpoint of improving image tone, of preventing the generation of interference fringes and of preventing irradiation on laser exposure, various types of dyes and pigments (for instance, C.I. Pigment Blue 60, C.I. Pigment Blue 64, and C.I. Pigment Blue 15:6) may be used in the photosensitive layer of the invention. Detailed description can be found in WO No. 98/36322, JP-A Nos. 10-268465 and 11-338098, and the like.

[0146]

In order to form an ultra-high contrast image suitable for use in graphic arts, it is preferred to add an ultra-high contrast promoting agent into the image forming layer. Details on the ultra-high contrast promoting agents, method of their addition and addition amount can be found in paragraph No. 0118, paragraph Nos. 0136 to 0193 of JP-A No. 11-223898, as compounds expressed by formulae (H), (1) to (3), (A), and (B) in Japanese Patent Application No. 11-87297, as compounds expressed by formulae (III) to (V) (specific compounds: Formula 21 to Formula 24) in Japanese Patent Application No. 11-91652; as an ultra-high contrast accelerator, description can be found in paragraph No. 0102 of JP-A No. 11-65021, and in paragraph Nos. 0194 to 0195 of JP-A No. 11-223898.

[0147]

In the case of using formic acid or formates as a strong fogging agent, it is preferably incorporated into the side having thereon the image forming layer containing photosensitive silver halide, in an amount of 5 mmol or less, preferably, one mmol or less per one mol of silver.

In the case of using an ultra-high contrast promoting agent in the photothermographic material of the invention, it is preferred to use an acid resulting from hydration of diphosphorus pentoxide, or its salt in combination. Examples of acids resulting from the hydration of diphosphorus pentoxide or salts thereof include metaphosphoric acid (salt), pyrophosphoric acid (salt), orthophosphoric acid (salt), triphosphoric acid (salt), tetraphosphoric acid (salt), hexametaphosphoric acid (salt), and the like. Particularly preferred acids obtainable by the hydration of diphosphorus pentoxide or salts thereof include orthophosphoric acid (salt) and hexametaphosphoric acid (salt). Specifically mentioned as the salts are sodium orthophosphate, sodium dihydrogen orthophosphate, sodium hexametaphosphate, ammonium hexametaphosphate, and the like.

The amount of usage of the acid obtained by hydration of diphosphorus pentoxide or the salt thereof (i.e., the coverage per 1 m<sup>2</sup> of the photosensitive material) may be set as desired depending on the sensitivity and fogging, but preferred is an amount of 0.1 mg/m<sup>2</sup> to 500 mg/m<sup>2</sup>, and more preferably, of 0.5 mg/m<sup>2</sup> to 100 mg/m<sup>2</sup>.

[0148]

### 13. Layer constitution and other constituting components

The photothermographic material according to the invention may have a non-photosensitive layer in addition to the image forming layer. The non-photosensitive layers can be classified depending on the layer arrangement into (a) a surface protective layer provided on the image forming layer (on the side farther from the support), (b) an intermediate layer provided among plural image forming layers or between the image forming layer and the protective layer, (c) an undercoat layer provided between the image forming layer and the support, and (d) a back layer provided to the side opposite to the image forming layer.

[0149]

Furthermore, a layer that functions as an optical filter may be provided as (a) or (b) above. An antihalation layer may be provided as (c) or (d) to the photosensitive material.

[0150]

#### 1) Surface protective layer

The photothermographic material of the invention may further comprise a surface protective layer with an object to prevent adhesion of the image forming layer. The surface

protective layer may be a single layer, or plural layers. Description on the surface protective layer may be found in paragraph Nos. 0119 to 0120 of JP-A No. 11-65021 and in Japanese Patent Application No. 2000-171936.

[0151]

As the binder of the surface protective layer, any polymer can be used. Examples of these binders include polyester, gelatin, polyvinylalcohol, and cellulose derivatives. Among these, cellulose derivatives are preferred. Examples of a cellulose derivative are set forth below, however, examples are not limited thereto. Examples of a cellulose derivative include cellulose acetate, cellulose acetate butyrate, cellulose propionate, hydroxypropyl cellulose, hydroxypropyl methylcellulose, methyl cellulose, hydroxyethyl methylcellulose, carboxymethyl cellulose and the mixtures thereof. The thickness of the surface protective layer is preferably 0.1 to 10  $\mu\text{m}$ , and particularly preferably 1 to 5  $\mu\text{m}$ .

[0152]

Any adhesion-preventing material may be used for the surface protective layer. Examples of the adhesion-preventing material include wax, liquid paraffin, silica particles, styrene-containing elastomeric block copolymers (such as styrene-butadiene-styrene and styrene-isoprene-styrene copolymers), cellulose acetate, cellulose acetate butylate, cellulose propionate and mixtures thereof.

[0153]

2) Antihalation layer

The photothermographic material of the present invention may comprise an antihalation layer provided to the side farther from the light source with respect to the photosensitive layer. Descriptions on the antihalation layer can be found in paragraph Nos. 0123 to 0124 of JP-A No. 11-65021, in JP-A Nos. 11-223898, 9-230531, 10-36695, 10-104779, 11-231457, 11-352625, 11-352626, and the like.

[0154]

The antihalation layer contains an antihalation dye having its absorption at the wavelength of the exposure light. In the case the exposure wavelength is in the infrared region, an infrared-absorbing dye may be used, and in such a case, preferred are dyes having no absorption in the visible region.

[0155]

In the case of preventing halation from occurring by using a dye having absorption in the visible region, it is preferred that the color of the dye would not substantially reside after image formation, and is preferred to employ a means for bleaching color by the heat of thermal development; in particular, it is preferred to add a thermal bleaching dye and a base precursor to the non-photosensitive layer to impart function as an antihalation layer. Those techniques are described in JP-A No. 11-231457 and the like.

[0156]

The amount of the thermal bleaching dye added is determined depending on the usage of the dye. In general, it is used in such an amount that the optical density (absorbance) exceeds 0.1 when measured at the desired wavelength. The optical density is preferably in a range of from 0.2 to 2. The usage of dyes to obtain optical density in the above range is generally from about 0.001  $\text{g}/\text{m}^2$  to 1  $\text{g}/\text{m}^2$ .

[0157]

By thermal bleaching the dye in such a manner, the optical density after thermal development can be lowered to 0.1 or lower. Two or more types of thermal bleaching dyes may be used in combination in a photothermographic material. Similarly, two or more types of base precursors may be used in combination.

[0158]

In thermal bleaching process using such a thermal bleaching dye and a base precursor, preferred is to use a substance (for instance, diphenylsulfone, 4-chlorophenyl(phenyl)sulfone, and the like) as disclosed in JP-A No. 11-352626, as well as 2-naphthyl benzoate and the like, which is capable of lowering the melting point of a base precursor by 3°C or more when mixed with a basic precursor from the viewpoint of thermal bleaching property or the like.

[0159]

3) Back layer

Back layers usable in the invention are described in paragraph Nos. 0128 to 0130 of JP-A No. 11-65021.

[0160]

Binders for the back layer are those that are transparent or translucent, and that are generally colorless, such as natural resin or polymer and their copolymers; synthetic resin or polymer and their copolymers; or media forming a film; for example, included are gelatin, gum arabic, poly(vinyl alcohol), hydroxyethyl cellulose, cellulose acetate, cellulose acetate butyrate, poly(vinyl pyrrolidone), casein, starch, poly(acrylic acid), poly(methylmethacrylic acid), poly(vinyl chloride), poly(methacrylic acid), styrene-maleic anhydride copolymers, styrene-acrylonitrile copolymers, styrene-butadiene copolymers, poly(vinyl acetal) (e.g., poly(vinyl formal) and poly(vinyl butyral)), poly(ester), poly(urethane), phenoxy resin, poly(vinylidene chloride), poly(epoxide), poly(carbonate), poly(vinyl acetate), cellulose esters, and poly(amide). The binder may be mixed with water or an organic solvent or may be formed as an emulsion for coating.

[0161]

In the invention, coloring matters having maximum absorption in the wavelength range of from 300 nm to 450 nm may be added in order to improve a color tone of developed images and a deterioration of the images during aging. Such coloring matters are described in, for example, JP-A Nos. 62-210458, 63-104046, 63-103235, 63-208846, 63-306436, 63-314535, 01-61745, 2001-100363, and the like. Such coloring matters are generally added in the range of from 0.1 mg/m<sup>2</sup> to 1 g/m<sup>2</sup>, preferably to the back layer provided to the side opposite to the photosensitive layer.

[0162]

4) Antistatic layer

The photothermographic material of the invention may contain an electrically conductive layer including various known metal oxides or electrically conductive polymers. The antistatic layer may serve as an undercoat layer, or a back surface protective layer, and the like, but can also be placed specially. Techniques described in JP-A Nos. 11-65021, 56-143430, 56-143431, 58-62646, and 56-120519, and in paragraph Nos. 0040 to 0051 of JP-A No. 11-84573, US-P No. 5575957, and in paragraph Nos. 0078 to 0084 of JP-A No. 11-223898 can be used for the antistatic layer.

[0163]

5) Additives

5-1) Matting agent

A matting agent may be preferably added to the photothermographic material of the invention in order to improve transportability. Description on the matting agent can be found in paragraph Nos. 0126 to 0127 of JP-A No.11-65021.

The amount of the matting agents added is preferably in the range from 1 mg/m<sup>2</sup> to 400 mg/m<sup>2</sup>, more preferably, from 5 mg/m<sup>2</sup> to 300 mg/m<sup>2</sup>, with respect to the coating amount per one m<sup>2</sup> of the photosensitive material.

[0164]

The matness on the emulsion surface is not restricted unless so-called star-dust trouble, in which small white spots are formed in image portions and light leaks are generated, occurs. However, the matness of 200 seconds to 10000 seconds is preferred, and the matness of 300 seconds to 8000 seconds is particularly preferred as Beck's smoothness. Beck's smoothness can be calculated easily, by seeing Japan Industrial Standard (JIS) P8119 "The method of testing Beck's smoothness for papers and sheets using Beck's test apparatus", or TAPPI standard method T479.

[0165]

The matt degree of the back layer in the invention is preferably in a range of 250 to 10 seconds; more preferably, 180 to 50 seconds, as expressed by Beck smoothness.

In the invention, the matting agent is incorporated preferably in the outermost surface layer on the photosensitive layer plane or a layer functioning as the outermost surface layer, or a layer near the outer surface, and a layer that functions as the so-called protective layer.

[0166]

The matting agent used in the invention is formed by organic or inorganic fine particles insoluble in a coating solvent. For example, those well known in the art such as organic matting agents described in U.S. Patent Nos. 1939213, 2701245, 2322037, 3262782, 3539344 and 3767448, and inorganic matting agents described in U.S. Patent Nos. 1260772, 2192241, 3257206, 3370951, 3523022 and 3769020 can be used. Specific examples of organic compounds which can be preferably used as the matting agents include water dispersible vinyl polymers such as polymethyl acrylate, polymethyl methacrylate, polyacrylonitrile, an acrylonitrile- $\alpha$ -methylstyrene copolymer, polystyrene, a styrene-divinylbenzene copolymer, polyvinyl acetate, polyethylene carbonate and polytetrafluoroethylene; cellulose derivatives such as methyl cellulose, cellulose acetate and cellulose propionate; starch derivatives such as carboxy starch, carboxynitrophenyl starch and a urea-formaldehyde-starch reaction product; gelatin hardened by a known hardening agent; and hardened gelatin formed by hardening coacervate to obtain microcapsules of hollow grains. Examples of preferable inorganic compounds include silicon dioxide, magnesium dioxide, aluminum oxide, barium sulfate, calcium carbonate, and silver chloride and silver bromide desensitized by known methods (such as glass or diatomaceous earth). The above matting agents may be used, if necessary, by being mixed with different kinds of materials. The size and the shape of the matting agent are not particularly limited, and the matting agent of any particle size can be used. In the invention, the matting agent having a particle size of 0.1  $\mu$ m to 30  $\mu$ m is preferably used. Further, the particle size distribution of the matting agent may be narrow or wide. Since the matting agent has a great effect on haze and surface gloss of the photosensitive material, the matting agent is preferably produced so as to have



desirable particle size, shape and particle size distribution, or a plurality of matting agents may be mixed to obtain desirable particle size, shape and particle size distribution.

[0167]

#### 5-2) Hardener

A hardener can be used in each of image forming layer, protective layer, back layer, and the like.

As examples of the hardener, descriptions of various methods can be found in pages 77 to 87 of T.H. James, "THE THEORY OF THE PHOTOGRAPHIC PROCESS, FOURTH EDITION" (Macmillan Publishing Co., Inc., 1977). Preferably used are chromium alum, sodium salt of 2,4-dichloro-6-hydroxy-s-triazine, N,N-ethylene bis(vinylsulfonacetamide), and N,N-propylene bis(vinylsulfonacetamide), polyvalent metal ions described in page 78 of the above literature and the like, polyisocyanates described in USP No. 4,281,060, JP-A No. 6-208193 and the like, epoxy compounds of USP No. 4,791,042 and the like, and vinyl sulfone based compounds of JP-A No. 62-89048. Particularly, vinyl sulfone based compounds are preferable, and nondiffusible vinyl sulfone compounds are more preferable.

[0168]

The hardener is added as a solution, and the solution is added to the coating solution for forming the protective layer 180 minutes before coating to just before coating, preferably 60 minutes before to 10 seconds before coating. However, so long as the effect of the invention is sufficiently exhibited, there is no particular restriction concerning the mixing method and the conditions of mixing.

[0169]

As specific mixing methods, there can be mentioned a method of mixing in the tank, in which the average stay time calculated from the flow rate of addition and the feed rate to the coater is controlled to yield a desired time, or a method using static mixer as described in Chapter 8 of N. Harnby, M.F. Edwards, A.W. Nienow (translated by Koji Takahashi) "Liquid Mixing Technology" (Nikkan Kogyo Shinbun, 1989), and the like.

[0170]

#### 5-3) Surface active agent

A surface active agent may be used in the photothermographic material of the invention in order to improve coating and charging properties. Any type of surface active agents, such as nonionic, anionic, cationic and fluorocarbon surface active agents, may be appropriately used. Specific examples include fluorocarbon high molecular surface active agents described in JP-A No. 62-170950 and U.S. Patent No. 5380644, a polysiloxane surface active agent described in U.S. Patent No. 3885965, and polyalkylene oxide or anionic surface active agents described in JP-A No. 6-301140.

[0171]

In the invention, preferably used are fluorocarbon surface active agents. Specific examples of preferable fluorocarbon surface active agents can be found in those described in JP-A Nos. 10-197985, 2000-19680, and 2000-214554. Polymer fluorocarbon surface active agents described in JP-A 9-281636 can be also used preferably. In the invention, the use of the fluorocarbon surface active agent described in Japanese Patent Application No. 2000-206560 is preferred.

#### 5-4) Other additives

Furthermore, an antioxidant, a stabilizing agent, a plasticizer, a UV absorbent, or a

coating aid may be added to the photothermographic material. Each of the additives is added to either the photosensitive layer or the non-photosensitive layer. Reference can be made to WO No. 98/36322, EP-A No. 803764A1, JP-A Nos. 10-186567 and 10-18568, and the like.

[0172]

6) Surface pH

The surface pH of the photothermographic material according to the invention is preferably 7.0 or lower, more preferably, 6.6 or lower, before thermal development treatment. Although there is no particular restriction concerning the lower limit, the pH value is about 3, and the most preferred surface pH range is from 4 to 6.2.

[0173]

From the viewpoint of reducing the surface pH, it is preferred to use an organic acid such as phthalic acid derivative or a non-volatile acid such as sulfuric acid, or a volatile base such as ammonia for the adjustment of the surface pH. In particular, ammonia can be used favorably for the achievement of low surface pH, because it can easily vaporize and can be removed before the coating step or before applying thermal development.

It is also preferred to use a non-volatile base such as sodium hydroxide, potassium hydroxide, lithium hydroxide, and the like, in combination with ammonia. The method of measuring a surface pH value is described in paragraph No. 0123 of the specification of Japanese Patent Application No. 11-87297.

[0174]

7) Support

Examples of the support include polyester films, undercoated polyester films, poly(ethylene terephthalate) films, polyethylene naphthalate films, cellulose nitrate films, cellulose ester films, poly(vinyl acetal) films, polycarbonate films and materials relevant thereto, resin materials, glass, paper, metal and the like. Further, a flexible base material, particularly partially acetylated paper, and baryta paper and/or paper coated with an  $\alpha$ -olefin copolymer, particularly polyethylene or polypropylene ( $\alpha$ -olefin copolymer having 2 to 10 carbon atoms such as an ethylene-butene copolymer) may also be used as the support. Although the support may be transparent or opaque, it is preferable that the support is transparent.

[0175]

As the transparent support, favorably used is polyester, particularly, polyethylene terephthalate, which is subjected to heat treatment in the temperature range of from 130°C to 185°C in order to relax the internal strain caused by biaxial stretching and remaining inside the film, and to remove strain ascribed to heat shrinkage generated during thermal development.

[0176]

In the case of a photothermographic material for medical use, the transparent support may be colored with a blue dye (for instance, dye-1 described in the example of JP-A No. 8-240877), or may be uncolored. A specific example of the support is described in paragraph No. 0134 of JP-A No. 11-65021.

[0177]

As to the support, it is preferred to apply undercoating technology, such as

undercoating of water-soluble polyester described in JP-A No. 11-84574, a styrene-butadiene copolymer described in JP-A No. 10-186565, a vinylidene chloride copolymer described in JP-A No. 2000-39684 and in paragraph Nos. 0063 to 0080 of Japanese Patent Application No. 11-106881, and the like.

[0178]

8) Coating method

The photothermographic material of the invention may be coated by any method. More specifically, various types of coating operations inclusive of extrusion coating, slide coating, curtain coating, immersion coating, knife coating, flow coating, or extrusion coating using the type of hopper described in USP No. 2,681,294 are used. Preferably used is extrusion coating or slide coating described in pages 399 to 536 of Stephen F. Kistler and Petert M. Schweizer, "LIQUID FILM COATING" (Chapman & Hall, 1997), and most preferably used is slide coating.

[0179]

8) Wrapping material

In order to suppress fluctuation from occurring on the photographic performance during a preservation of the photothermographic material of the invention before thermal development, or in order to improve curling or winding tendencies when the photothermographic material is in the form of a roll, it is preferred that the photothermographic material is sealed by a wrapping material having low oxygen transmittance and/or vapor transmittance. Preferably, oxygen transmittance is 50 ml/atm·m<sup>2</sup>·day or lower at 25°C, more preferably, 10 ml/atm·m<sup>2</sup>·day or lower, and most preferably, 1.0 ml/atm·m<sup>2</sup>·day or lower. Preferably, vapor transmittance is 10 g/atm·m<sup>2</sup>·day or lower, more preferably, 5 g/atm·m<sup>2</sup>·day or lower, and most preferably, 1 g /atm·m<sup>2</sup>·day or lower. As specific examples of a wrapping material having low oxygen transmittance and/or vapor transmittance, reference can be made to, for instance, the wrapping material described in JP-A Nos.8-254793 and 2000-206653.

[0180]

10) Other applicable techniques

Techniques which can be used for the photothermographic material of the invention also include those in EP803764A1, EP883022A1, WO98/36322, JP-A Nos. 56-62648, 58-62644, JP-A Nos. 09-43766, 09-281637, 09-297367, 09-304869, 09-311405, 09-329865, 10-10669, 10-62899, 10-69023, 10-186568, 10-90823, 10-171063, 10-186565, 10-186567, 10-186569 to 10-186572, 10-197974, 10-197982, 10-197983, 10-197985 to 10-197987, 10-207001, 10-207004, 10-221807, 10-282601, 10-288823, 10-288824, 10-307365, 10-312038, 10-339934, 11-7100, 11-15105, 11-24200, 11-24201, 11-30832, 11-84574, 11-65021, 11-109547, 11-125880, 11-129629, 11-133536 to 11-133539, 11-133542, 11-133543, 11-223898, 11-352627, 11-305377, 11-305378, 11-305384, 11-305380, 11-316435, 11-327076, 11-338096, 11-338098, 11-338099, 11-343420, Japanese Patent Application Nos. 2000-187298, 2000-10229, 2000-47345, 2000-206642, 2000-98530, 2000-98531, 2000-112059, 2000-112060, 2000-112104, 2000-112064 and 2000-171936.

[0181]

11) Formation of color image

A multi-color photothermographic material may be constituted so as to include a combination of these two layers for each color. Alternatively, all ingredients may be included into a single layer as described in USP No. 4,708,928.

In instances of multi-color photothermographic materials, each emulsion layer is, in general, held distinctively from each other by using a functional or nonfunctional barrier layer between each photosensitive layer as described in USP No. 4,460,681.

[0182]

14. Image forming method

1) Exposure

Although the photosensitive material of the invention may be subjected to exposure by any methods, laser beam is preferred as an exposure light source. Particularly, silver halide emulsion of high content of silver iodide had a problem of low photosensitivity, but this problem was solved with the use of high illumination intensity like laser beam. And it made clear that it needs a small amount of energy to record an image. Using thus strong light in a short time made it possible to achieve desired photosensitivity.

[0183]

Especially, for giving the exposure intensity to provide maximum density ( $D_{max}$ ), the light intensity on the surface of the photosensitive material is preferably in the range of  $0.1 \text{ W/mm}^2$  to  $100 \text{ W/mm}^2$ , more preferably  $0.5 \text{ W/mm}^2$  to  $50 \text{ W/mm}^2$ , most preferably  $1 \text{ W/mm}^2$  to  $50 \text{ W/mm}^2$ .

[0184]

As Laser beam according to the invention, preferably used are gas laser ( $\text{Ar}^+$ , He-Ne, He-Cd), YAG laser, pigment laser, semiconductor laser. Semiconductor laser and second harmonics generator element can also be used. Preferred laser is determined corresponding to the peak absorption wavelength of spectral sensitizer and the like, but preferred is He-Ne laser of red through infrared emission, red semiconductor laser, or  $\text{Ar}^+$ , He-Ne, He-Cd laser of blue through green emission, blue semiconductor laser. Meanwhile, modules having SHG (Second Harmonic Generator) chip and semiconductor laser which are integrated, or blue semiconductor laser have been especially developed recently, and thus laser output devices for short wavelength region have attracted the attention. Blue semiconductor laser has been expected as a light source with increasing demand hereafter because image recording with high definition is possible, and increased recording density, as well as stable output with longer operating life are enabled.

[0185]

Laser beam which oscillates in a longitudinal multiple modulation by a method such as high frequency superposition is also preferably employed.

[0186]

2) Thermal development

Although the development of the photothermographic material of the invention is usually performed by elevating the temperature of the photothermographic material exposed imagewise, any method may be used for this thermal development process. The temperature for the development is preferably  $80^\circ\text{C}$  to  $250^\circ\text{C}$ , preferably  $100^\circ\text{C}$  to  $140^\circ\text{C}$ , and more preferably  $110^\circ\text{C}$  to  $130^\circ\text{C}$ . Time period for the development is preferably 1 second to 60 seconds, more preferably 3 seconds to 30 seconds, particularly preferably 5 seconds to 25 seconds, and most preferably 7 seconds to 15 seconds.

[0187]

In the process for the thermal development, either drum type heaters or plate type

heaters may be used. However, plate type heater processes are more preferred. Preferable process for the thermal development by a plate type heater may be a process described in JP-A No. 11-133572, which discloses a thermal developing device in which a visible image is obtained by bringing a photothermographic material with a latent image into contact with a heating means at a thermal development region, wherein the heating means comprises a plate heater, and a plurality of retainer rollers are oppositely provided along one surface of the plate heater, the thermal developing device being characterized in that thermal development is performed by passing the photothermographic material between the retainer rollers and the plate heater. It is preferred that the plate heater is divided into 2 to 6 sections, with the leading end having a temperature lowered by 1 to 10°C. For example, 4 sets of plate heaters which can be independently subjected to the temperature control are used, and are controlled so that they respectively become 112°C, 119°C, 121°C, and 120°C. Such a process is also described in JP-A No. 54-30032, which allows for excluding moisture and organic solvents included in the photothermographic material out of the system, and also allows for suppressing the change of shapes of the support of the photothermographic material upon rapid heating of the photothermographic material.

[0188]

In the present invention, it is preferable to thermal-develop the photothermographic material while conveying the same at a processing rate of not less than 23 mm/sec. Fig. 1 shows a thermal developing device preferable in the invention.

The line velocity of development is the speed at which the photothermographic material passes between the presser roller and the plate heater.

[0189]

In the present invention, the distance between the exposing section and the developing section is 0 to 50 cm, thereby reducing processing time of the series of exposure and development remarkably. The distance is preferably 3 cm to 40 cm, and more preferably 5 cm to 30 cm.

The exposing section is a position at which the photothermographic material is irradiated with light from an exposure light source. The developing section is a position at which the photothermographic material is first heated for thermal development. X in Fig. 2 is the exposing section, and Y, at which the photosensitive material conveyed from 53 in Fig. 1 contacts a plate 51a for the first time, is the developing section.

[0190]

Because the exposing section and the developing section are disposed close to each other, a sheet begins to be developed at an exposed portion thereof while another portion is still exposed. In this image forming method in which the sensitive material is exposed at a portion and developed at another portion at the same time, because vibration of the sensitive material during conveyance has a direct effect on image quality, a photothermographic material that is not likely to be affected by vibration has been required.

Further, reducing the time required for exposure and development by conveying the photosensitive material at high speed, such as at a line velocity of 23 mm/sec or more, has been studied. When conveyed at such high speed, the photothermographic material is likely to be subjected to vibration. In this case, as in the case in which the exposing section and the developing section are disposed close to each other, there has been a demand for a photothermographic material that is less likely to be subjected to vibration.

[0191]

These problems were solved quickly by using a photothermographic material of our invention, in which color tone of the image is adjusted. Further, the above image forming method has an advantage of enabling further reduction in the processing time, and thus may be used increasingly.

[0192]

#### 15. System

Examples of a medical laser imager equipped with a light exposing part and a thermal developing part include Fuji Medical Dry Laser Imager FM-DP L. In connection with the FM-DPL, description is found in Fuji Medical Review No. 8, pages 39-55. It goes without mentioning that those techniques may be applied as the laser imager for the photothermographic material of the invention. In addition, the present photothermographic material can be also applied as a photothermographic material for the laser imager used in "AD network" which was proposed by Fuji Film Medical Co., Ltd. as a network system accommodated to DICOM standard.

[0193]

#### 16. Application of the invention

The image forming method in which the photothermographic material of the invention is used is preferably employed as an image forming method for photothermographic materials for use in medical imaging, photothermographic materials for use in industrial photographs, photothermographic materials for use in graphic arts, as well as for COM, through forming black and white images by silver imaging.

[0194]

#### [Examples]

The present invention is specifically explained by way of Examples below, which should not be construed as limiting the invention thereto.

[0195]

#### Example 1

##### 1. Preparation of PET Support and Undercoating

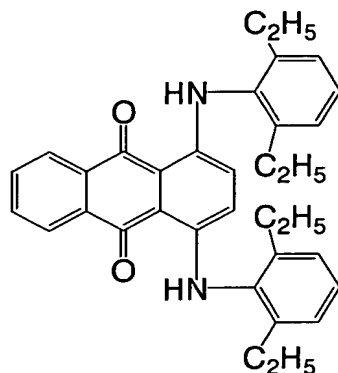
##### 1-1. Film Manufacturing

[0196]

PET having IV (intrinsic viscosity) of 0.66 (measured in phenol/tetrachloroethane = 6/4 (weight ratio) at 25°C) was obtained according to a conventional manner using terephthalic acid and ethylene glycol. The product was pelletized, dried at 130°C for 4 hours, melted at 300°C, and the dye BB having the following structure was included in an amount of 0.04% by weight. Thereafter, the mixture was extruded from a T-die and rapidly cooled to form a non-tentered film having such a thickness that the thickness should become 175 µm after tentered and thermal fixation.

[0197]

[Formula 19]



Dye BB

[0198]

The film was stretched along the longitudinal direction by 3.3 times using rollers of different peripheral speeds, and then stretched along the transverse direction by 4.5 times using a tenter machine. The temperatures used for these operations were 110°C and 130°C, respectively. Then, the film was subjected to thermal fixation at 240°C for 20 seconds, and relaxed by 4% along the transverse direction at the same temperature. Thereafter, the chucking part was slit off, and both edges of the film were knurled. Then the film was rolled up at the tension of 4 kg/cm<sup>2</sup> to obtain a roll having the thickness of 175 μm.

[0199]

#### 1-2. Surface Corona Discharge Treatment

Both surfaces of the support were treated at room temperature at 20 m/minute using Solid State Corona Discharge Treatment Machine Model 6KVA manufactured by Piller GmbH. It was proven that treatment of 0.375 kV·A·minute/m<sup>2</sup> was executed, judging from the readings of current and voltage on that occasion. The frequency upon this treatment was 9.6 kHz, and the gap clearance between the electrode and dielectric roll was 1.6 mm.

[0200]

#### 2. Preparation and Coating of Coating Solution for Back Layer

To 830 g of MEK were added 84.2 g of cellulose acetate butyrate (Eastman Chemical, CAB381-20) and 4.5 g of a polyester resin (Bostic Co., Vitel PE2200B) with stirring, and dissolved. To this dissolved solution was added 0.30 g of dye-1, and thereto were added 4.5 g of a fluorocarbon surfactant (Asahi Glass Co., Ltd., Surflon HK40) which had been dissolved in 43.2 g of methanol, and 2.3 g of a fluorocarbon surfactant (Dai-Nippon Ink & Chemicals, Inc., Megafac(R) F120K). The mixture was thoroughly stirred until dissolution was completed. Finally, 75 g of silica (W. R. Grace Co., Siloid 64X6000) dispersed in methyl ethyl ketone at a concentration of 1% by weight with a dissolver type homogenizer was added thereto followed by stirring to prepare a coating solution for the back layer.

[0201]

Thus prepared coating solution for the back layer was coated on the support with an extrusion coater so that the dry film thickness became 3.5 μm and dried. Drying was executed by a hot air with a temperature of 100°C, and a dew point of 10°C over 5 minutes.

[0202]

#### 3. Image-Forming Layer and Surface Protective Layer

##### 3-1. Preparation of Materials for Coating

### 1) Silver Halide Emulsion

#### (Preparation of Silver Halide Emulsion-1)

To 1420 mL of distilled water was added 3.1 mL of a 1% by mass potassium bromide solution. Further, a liquid added with 3.5 mL of sulfuric acid having the concentration of 0.5 mol/L and 31.7 g of phthalated gelatin was kept at 27°C while stirring in a stainless steel reaction pot, and thereto were added total amount of: solution A prepared through diluting 22.22 g of silver nitrate by adding distilled water to give the volume of 95.4 mL; and solution B prepared through diluting 15.3 g of potassium bromide and 0.8 g of potassium iodide with distilled water to give the volume of 97.4 mL, over 45 seconds at a constant flow rate. Thereafter, 10 mL of a 3.5% by mass aqueous solution of hydrogen peroxide was added thereto, and 10.8 mL of a 10% by mass aqueous solution of benzimidazole was further added. Moreover, a solution C prepared through diluting 51.86 g of silver nitrate by adding distilled water to give the volume of 317.5 mL and a solution D prepared through diluting 44.2 g of potassium bromide and 2.2 g of potassium iodide with distilled water to give the volume of 400 mL were added. A controlled double jet method was executed through adding total amount of the solution C at a constant flow rate over 20 minutes, accompanied by adding the solution D while maintaining the pAg at 8.1.

[0203]

Hexachloroiridium (III) potassium salt was added to give  $1 \times 10^{-4}$  mol per one mol of silver 10 minutes after initiation of the addition of the solution C and the solution D in its entirety. Moreover, 5 seconds after completing the addition of the solution C, a potassium iron (II) hexacyanide aqueous solution was added in a total amount of  $3 \times 10^{-4}$  mol per one mol of silver. The mixture was adjusted to the pH of 3.8 with sulfuric acid at the concentration of 0.5 mol/L. After stopping stirring, the mixture was subjected to precipitation, desalting and water washing steps. The mixture was adjusted to the pH of 5.9 with sodium hydroxide at the concentration of one mol/L to produce a silver halide dispersion having the pAg of 8.0. Grains in thus prepared silver halide emulsion were silver iodide bromide grains having a mean sphere equivalent diameter of 0.035  $\mu\text{m}$ , a variation coefficient of 15%, which uniformly include iodine at 3.5 mol%. Grain size and the like were determined from the average of 1000 grains using an electron microscope.

[0204]

The silver halide dispersion was kept at 38°C with stirring, and thereto was added 5 mL of a 0.34% by mass methanol solution of 1,2-benzisothiazoline-3-one, followed by elevating the temperature to 47°C. 20 minutes after elevating the temperature, sodium benzene thiosulfonate in a methanol solution was added in an amount of  $7.6 \times 10^{-5}$  mol per one mol of silver, and then pAg was adjusted to 5.5. Additional 5 minutes later, a tellurium sensitizer C in a methanol solution was added in an amount of  $2.9 \times 10^{-4}$  mol per one mol of silver and subjected to aging for 91 minutes. After adjusting pAg of the emulsion to 7.5, 1.3 mL of a 0.8% by mass N,N'-dihydroxy-N'',N''-diethylmelamine in methanol was added thereto, and additional 4 minutes thereafter, 5-methyl-2-mercaptobenzimidazole in a methanol solution in an amount of  $4.8 \times 10^{-3}$  mol per one mol of silver, 1-phenyl-2-heptyl-5-mercapto-1,3,4-triazole in a methanol solution in an amount of  $5.4 \times 10^{-3}$  mol per one mol of silver, and 1-(3-methylureidophenyl)-5-mercaptotetrazole in an aqueous solution in an amount of  $8.5 \times 10^{-3}$  mol per one mol of silver were added to produce a silver halide emulsion-1.

[0205]

#### (Preparation of Silver Halide Emulsion-2 and Silver Halide Emulsion-3)

Preparations of silver halide emulsion-2 and -3 were conducted in a similar manner



to the process in the preparation of the silver halide emulsion-1 except that: the temperature of the liquid upon the nucleation process was altered from 27°C to 35°C or 47°C.

The mean sphere equivalent diameter of the emulsion grains in the silver halide emulsion-2 was 0.055 µm, and that of the grains in the silver halide emulsion-3 was 0.080 µm.

[0206]

2) Preparation of silver salts of fatty acid

<<Preparation of Silver Salt of Fatty Acid-1>>

To 4720 mL of purified water were added behenic acid, arachidic acid, and stearic acid in an amount of 0.7552 mol in total with a ratio 42 mol%, 34 mol% and 24 mol%, respectively. After dissolving at 80°C, 540.2 mL of a 1.5 N aqueous NaOH solution was added to the solution, and thereto was added 6.9 mL of concentrated nitric acid, followed by cooling to 55°C to obtain a solution of sodium salt of organic acid. While keeping the temperature of the sodium salt of organic acid solution at 55°C, 45.3 g of the aforementioned silver halide emulsion and 450 mL of purified water were added thereto. The mixture was stirred with a homogenizer manufactured by IKA JAPAN Co. (ULTRA-TURRAXT-25) at 13200 rpm (corresponding to 21.1 kHz of mechanical vibration frequency) for 5 minutes. Then, 702.6 mL of a 1 mol/L silver nitrate solution was added thereto over 2 minutes, followed by stirring for 10 minutes to obtain an organic silver salt dispersion. Thereafter, the resulting organic silver salt dispersion was transferred to a washing vessel, and thereto was added deionized water followed by stirring. The mixture was allowed to stand still so that the organic silver salt dispersion was floatated, and thus water soluble salts present in the bottom part were removed. Then, washing with deionized water and drainage of the waste water was repeated until the electric conductivity of the waste water became 2 µS/cm. After performing centrifugal dewatering, drying in a circulating dryer was performed with warm air having the oxygen partial pressure of 10% by volume at 40°C until weight loss did not take place to obtain the silver salt of fatty acid-1 including photosensitive silver halide.

[0207]

<<Preparation of Silver Salts of Fatty Acid-2 and -3>>

Preparation of silver salts of fatty acids-2 and -3 was conducted in a similar manner to the process in the preparation of the silver salt of fatty acid-1 except using silver halide emulsion-2 and -3, instead of using silver halide emulsion-1.

[0208]

<<Preparations of Silver Salts of Fatty Acid-4 to -7>>

Preparation of silver salts of fatty acid-4 to -7 was conducted in a similar manner to the process in the preparation of the silver salt of fatty acid-1 except using silver halide emulsion-1 to -3 with a ratio presented in Table 1, instead of using silver halide emulsion-1.

[0209]

3) Redispersion of Organic Silver Salts in Organic Solvent

<<Preparation of Organic Silver Salt Redispersion-1>>

209 g of powdery silver salt of fatty acid-1 mentioned above and polyvinyl butyral powder (Monsanto Co., Butvar B-79) in an amount of 11 g were dissolved in 780 g of methyl ethyl ketone (MEK) while stirring with Dissolver DISPERMAT CA-40M type manufactured by VMA-GETZMANN Co., and then cooled overnight at 7 °C to yield a slurry. The slurry was subjected to two passes dispersion with a GM-2 pressure type homogenizer manufactured by SMT Limited to prepare an organic silver salt redispersion-1.

[0210]

<<Preparation of Organic Silver Salt Redispersions-2 to -7>>

Preparation of organic silver salt redispersions-2 to -7 was conducted in a similar manner to the process in the preparation of the organic silver salt redispersion-1 except using silver salts of fatty acid-2 to -7, instead of using silver salt of fatty acid-1.

[0211]

4) Preparation of Coating Solutions for Image Forming Layer-1 to -7

Either one of the organic silver salt redispersions-1 to -7 mentioned above including photosensitive silver halide in an amount of 507 g, was stirred for 15 minutes at 13°C, and thereto was added 3.9 mL of a 10% by mass methanol solution of pyridinium bromide perbromide (PHP). After stirring for 2 hours, thereto was added 5.2 mL of a 72% by mass methanol solution of calcium bromide. The mixture was subsequently stirred for 30 minutes, thereto was added 117 g of Butvar B-79. After stirring for 30 minutes, 27.3 g of reducing agent (R-2) was added to the mixture, followed by stirring for 15 minutes. Then, thereto was added sensitizing dye-1 in an amount of  $1 \times 10^{-3}$  mol per one mol of silver halide followed by stirring for 15 minutes. Then was subsequently added 1.39 g of Desmodur N3300 (Mobay, aliphatic isocyanate) dissolved to 12.3 g of MEK, and stirred for additional 15 minutes, and then heated to 21°C for 15 minutes.

[0212]

Further, to 100 g of this dispersion was added polyhalide compound-1 in amount of 0.03 mol per one mol of coated silver, FED sensitizer-1, -2, and -3 in amount of  $2 \times 10^{-3}$  mol each per one mol of silver halide, hydrogen bonding compound-1 in the same mol amount as reducing agent, development accelerator-1 and -2 each in an amount of  $5 \times 10^{-3}$  mol per one mol of silver salt of fatty acid, 2.2g of 4-chlorobenzophenone-2-carboxylic acid, 0.47 g of 2-chlorobenzoic acid, and 0.47 g of 5-methyl-2 mercaptobenzimidazole, followed by stirring for one hour at 21 °C. Then, thereto was added 0.368 g of phthalazine, 0.123 g of tetrachlorophthalic acid and 2 g of dye-1 to obtain coating solutions for image forming layer-1 to -7.

[0213]

5) Preparation of Coating Solution for Surface Protective Layer

In 865 g of MEK were mixed, while stirring, 96 g of cellulose acetate butyrate (Eastman Chemical, CAB171-15S), 4.5 g of polymethyl methacrylic acid (Rohm and Haas, Acryloid A-21), 1.5 g of 1,3-di(vinylsulfonyl)-2-propanol, 1.0 g of benzotriazole, and 1.0 g of a fluorocarbon polymersurfactant (Asahi Glass Co., Ltd., Surflon HK40), and thoroughly dissolved. Thereto was added 30 g of the dispersion prepared by dispersing 13.6% by mass of cellulose acetate butylate (Eastman Chemical, CAB171-15) and 9% by mass of calcium carbonate (Speciality Minerals, Super-Pflex) to MEK using disolver type homogenizer at 8000 rpm for 30 minutes followed by stirring to prepare a coating solution for the surface protective layer-1.

[0214]

3-2. Preparation of Photothermographic Materials

Photothermographic materials-1 to -7 were prepared by simultaneous double coating of either one of the coating solutions for image forming layer prepared as shown above, and the coating solution for the surface protective layer using a dual knife coater, on a reverse surface to the back layer of the support coated with the back layer. The coating was

executed so that the image forming layer had the thickness after drying of 18.3  $\mu\text{m}$ , and that the surface protective layer had the dry film thickness of 3.4  $\mu\text{m}$ . This coating device has two knife coating blades which are laid side by side. After cutting the support to the size so that it meets with the volume of the solution used, knives equipped with a hinge were elevated to put them in a position on the coater floor. Then, the knives were brought down and fixed onto a predetermined position. The height of the knives was regulated using a wedge which was measured with an ammeter and which was controlled by a screw knob. Knife #1 was elevated up to a clearance corresponding to the thickness which was coordinated with total thickness of the substrate thickness and the desired wet thickness of the image forming layer (layer #1). Knife #2 was elevated up to the height equal to the total thickness of: support thickness + wet thickness of the image forming layer (layer #1) + desired thickness of the surface protective layer (layer #2). Thereafter, drying was performed with an air of the temperature of 75°C and a dew point of 10°C for 15 minutes.

In the case, the image forming layer is made of two layers, three knife coating blades are used, and the coating was executed so that the thickness after drying of each of the upper and the lower image forming layer becomes 9.15  $\mu\text{m}$ . Preparation of photothermographic materials-8 to -12 was conducted this way.

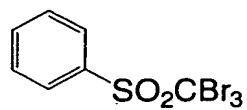
[0215]

Chemical structures of the compounds used in Examples of the invention are shown below.

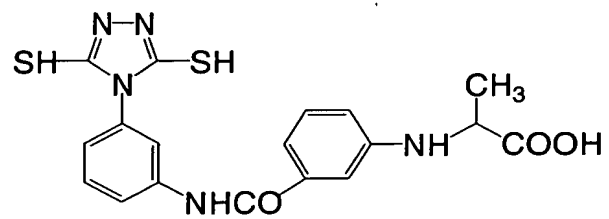
[0216]

[Formula 20]

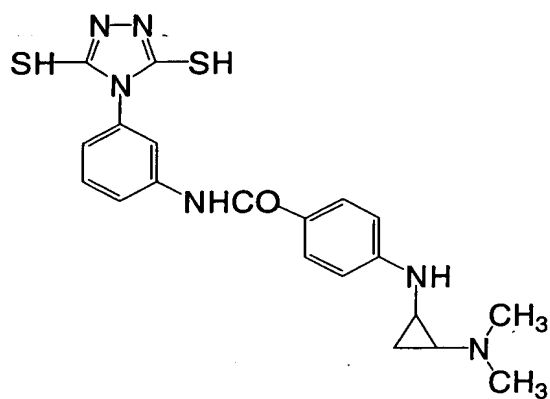
Polyhalogen Compound-1



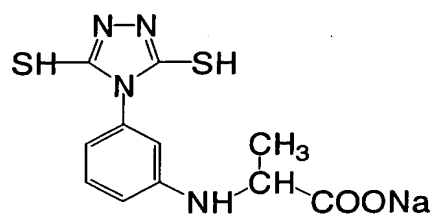
FED Sensitizer-1



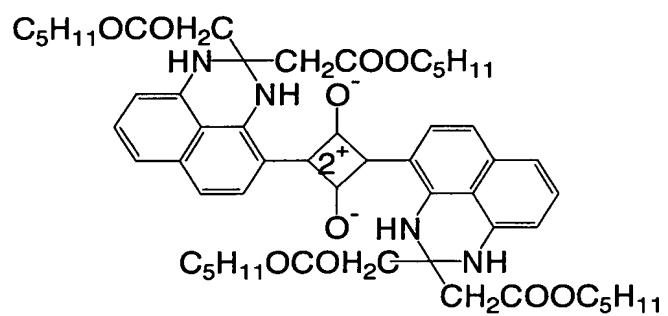
FED Sensitizer-2



FED Sensitizer-3



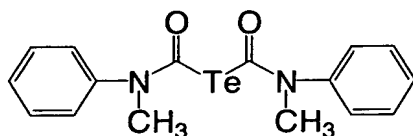
Dye-1



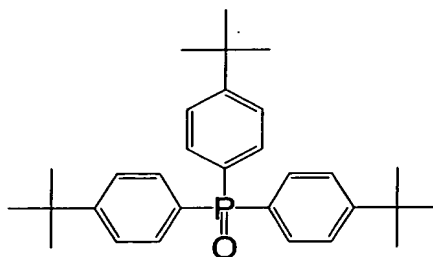
[0217]

[Formula 21]

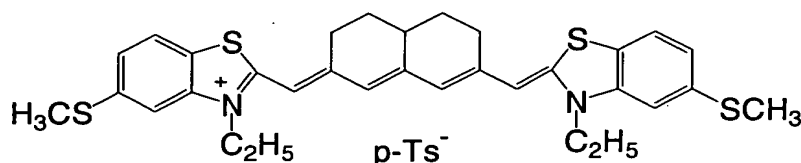
Tellurium Sensitizer C



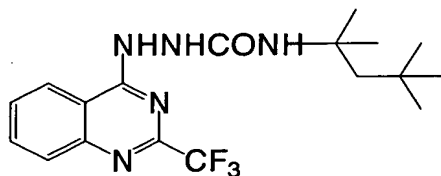
Hydrogen Bonding Compound-1



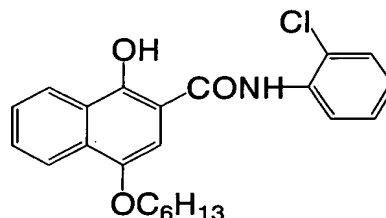
Sensitizing Dye-1



Development Accelerator-1



Development Accelerator-2



[0218]

#### 4. Evaluation of Photographic Performances

##### (Preparation)

The resulting sample was cut into a half-cut size (43 cm in length x 35 cm in width), and was wrapped with the following packaging material under an environment of 25°C and 50% RH, and stored for 2 weeks at an ambient temperature.

##### (Packaging Material)

PET 10 μm/ PE 12 μm/ aluminum foil 9 μm/ Ny 15 μm/ polyethylene 50 μm containing carbon at 3% by weight, oxygen permeability: 0.02 mL/atm·m<sup>2</sup>·25°C·day, vapor permeability: 0.10 g/atm·m<sup>2</sup>·25°C·day.

[0219]

The above photosensitive materials were evaluated as follows.

##### (Exposure and Development of Photosensitive Materials)

An exposure machine was manufactured by way of trial, with semiconductor laser, which was longitudinally multiple modulated at the wavelength of 800 nm through 820 nm with high frequency superposition, as an exposure light source. Exposure was provided by laser scanning using this exposure machine to the image forming layer surface side of the samples-1 to -25 prepared as described hereinbefore. Upon the exposure, images were recorded with an incident angle of the scanning laser beam to the surface of the

photothermographic material set to be 75°. After the exposure, thermal development was performed using an automated developing apparatus including heat drum, the protective layer of the photothermographic material being in contact with the surface of the drum, with the development temperature set to be 124°C and total development time period of 15 seconds. Evaluation of thus resulting images was carried out with a densitometer. In this process, the distance between the exposure section and the development section was 15 cm and the line speed of the photothermographic materials upon the thermal development was 21.3 mm/sec.

[0220]

(Evaluation of photographic properties)

1. Evaluation of image quality

The minimum density  $D_{min}$  was obtained by measuring the image of each of the photothermographic materials with Macbeth densitometer TD 904 (the visual density), and the uniform image was developed at the exposure value to give the optical density of  $D_{min} + 1.2$ , so that the uniformity of the density and the color tone of the silver images was evaluated and ranked to 4 levels:

- A: the excellent images with a high uniformity and the best color tone,
- B: better images having a slight irregularity in a density and an image color tone,
- C: images having an irregularity in a density and an image color tone, which may be allowable to be used practically in a market,
- D: images having an actual irregularity in a density and an image color tone, which may be troubled to be used practically in a market.

[0221]

2. Calculation of gamma value

A gamma value was calculated by measuring an optical density of the developed photothermographic materials. A gamma value obtained at an optical density of 1.2 in a characteristic curve during heating and development of the photothermographic material was indicated. The photographic characteristic curve is a D-log E curve, where the abscissa is an optical density (a photographic diffuse density  $D$ ), and the abscissa is a logarithmic value of an exposure amount which is an exposure energy ( $\log E$ ). The gamma ( $\gamma$ ) value is a gradient of a tangent at an optical density of 1.2 in the photographic characteristic curve, that is a  $\tan \theta$  where  $\theta$  is an angle between the tangent and the horizontal axis.

[0222]

[Table 1]

Photothermo-graphic material	Silver halide emulsion	$\gamma$ value	Result of evaluation	Dmax	Remarks
1	1	5	D	4.5	Comparative Example
2	2	4.3	C	3.5	Comparative Example
3	3	3.8	B	2.5	Present invention
4	1+2 (9:1)	3.5	B	4.4	Present invention
5	1+3 (9:1)	3	A	4.3	Present invention
6	2+3 (9:1)	3.3	B	3.5	Present invention
7	1+2+3 (8:1:1)	2.8	A	4.2	Present invention
8	upper layer:2 lower layer:1	3.2	A	4.4	Present invention
9	upper layer:3 lower layer:2	3	A	3.5	Present invention
10	upper layer:3 lower layer:1	2.7	A	4.3	Present invention
11	upper layer:2+3 lower layer:1+2	2.6	A	4.2	Present invention
12	upper layer:1+2+3 lower layer:1+2	2.5	A	4	Present invention

[0223]

As shown in Table 1, the developed images having a gamma of 2.0 to 4.0 were excellent in uniform density.

Among them, especially excellent results were obtained when the gamma value was 2.0 to 3.2.

[0224]

Example 2

The photothermographic materials were exposed and developed in a similar manner to that in Example 1 except that the line speed in the development was 28.6 mm/sec, and were evaluated in similar manner to that in Example 1 to obtain the similar results.

In the case the line speed was raised to over 23 mm/sec, the developed images having a  $\gamma$  value of 2.0 to 4.0 were excellent in uniform density.

[0225]

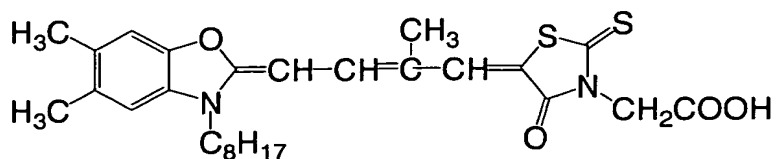
Example 3

Coating solutions for the image forming layer-13 to -19 were prepared in the similar manner to that in Example 1 except that sensitizing dye-2 was used instead of sensitizing dye-1 in the preparation of solutions for the image forming layer-1 to -7.

[0226]

[Formula 22]

### Sensitizing Dye-2



[0227]

Using coating solutions for the image forming layer-13 to -19, the photothermographic material-13 to -19 having one image forming layer and the photothermographic material-20 to -24 having a two-layered image forming layer were prepared in the similar manner to Example 1.

[0228]

(Exposure and Development of Photothermographic Materials)

Exposure and thermal development (14 seconds in total with 4 panel heaters set to be 112°C - 119°C - 121°C - 121°C) with Fuji Medical Dry Laser Imager FM-DP L (equipped with 660 nm semiconductor laser having the maximum output of 60 mW (IIIB)) reconstructed to raise the line speed of the development section were performed on the photothermographic material-13 to -24 obtained as described above. The line speed in this process was 29.3 mm/sec.

[0229]

(Evaluation of Photographic Performances)

Evaluations were carried out in the similar manner to those of Example 1. The results are shown in Table 2.

[0230]

[Table 2]



Photothermo-graphic material	Silver halide emulsion	$\gamma$ value	Result of evaluation	Dmax	Remarks
13	1	4.9	D	4.7	Comparative Example
14	2	4.2	C	3.7	Comparative Example
15	3	3.7	B	2.7	Present invention
16	1+2 (9:1)	3.4	B	4.6	Present invention
17	1+3 (9:1)	2.9	A	4.5	Present invention
18	2+3 (9:1)	3.2	A	3.7	Present invention
19	1+2+3 (8:1:1)	2.7	A	4.4	Present invention
20	upper layer:2 lower layer:1	3.1	A	4.6	Present invention
21	upper layer:3 lower layer:2	2.9	A	3.7	Present invention
22	upper layer:3 lower layer:1	2.6	A	4.5	Present invention
23	upper layer:2+3 lower layer:1+2	2.5	A	4.4	Present invention
24	upper layer:1+2+3 lower layer:1+2	2.4	A	4.2	Present invention

As shown in Table 2, the results were excellent similarly to Example 1 and the developed images having a gamma value of 2.0 to 4.0 were excellent in uniform density, even in the case the sensitizing dye was changed to sensitizing dye-2 for red laser beam and imagewise exposure was done by a red laser beam.

[0230]

Example 4

1) Redispersion of Organic Silver Salt in Organic Solvent

The slurries were dispersed with a media type dispersion machine packed with 80% by volume of 1-mm Zr beads (manufactured by Toray) at a circumferential velocity of 13 m, and retention time of 0.5 minutes in the similar manner to the redispersion of silver salt of fatty acid in Example 1 except that the slurries of silver salt of fatty acid-1 to -7 were subjected to two passes dispersion with a GM-2 pressure type homogenizer manufactured by SMT Limited, to obtain organic silver salt dispersion-1 to -7 including photosensitive silver halide.

[0231]

2) Preparation of Coating Solution for Image Forming Layer-25 to -31

Using 500 g of each of the aforementioned photosensitive silver halide containing organic silver salt dispersion-1 to -7, 100 g of methyl ethyl ketone (MEK) was added thereto while stirring under a nitrogen gas stream, and incubated at 24°C. The antifoggant-1 as described below (2.5 mL of a solution containing 10% by mass of the antifoggant-1 in methanol) was added thereto followed by stirring for 15 minutes. Thereto was added 1.8 mL of a 1 : 5 mixed solution of the following dye adsorption promotor and potassium acetate (a solution containing 20% by mass of the dye adsorption promotor), followed by stirring for 15 minutes. Next, sensitizing dye-3 in amount of  $1 \times 10^{-3}$  mol per one mol of silver halide, 7

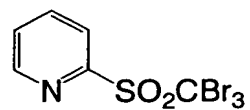
mL of a mixed solution of 4-chloro-2-benzoylbenzoic acid and super-sensitizer (5-methyl-2-mercaptobenzimidazole), with a mixing ratio of 25 : 2 by mass, polyhalide compound-2 in amount of 0.03 mol per one mole of coated silver, FED sensitizer-1, -2, and -3 each in an amount of  $2 \times 10^{-2}$  mol per one mol of silver halide, hydrogen bonding compound 1 in the same mol amount of reducing agent-1, and development accelerator-1 and -2 each in an amount of  $5 \times 10^{-3}$  mol per one mol silver of silver salt of fatty acid were added, followed by stirring for 1 hour. Thereafter, the temperature was lowered to 13°C, and the mixture was further stirred for 30 minutes. To this mixture was added 48 g of polyvinyl butyral while keeping the temperature at 13°C. After allowing for sufficient dissolution, the following additives were added. All of these operations were performed under a nitrogen gas stream.

[0232]

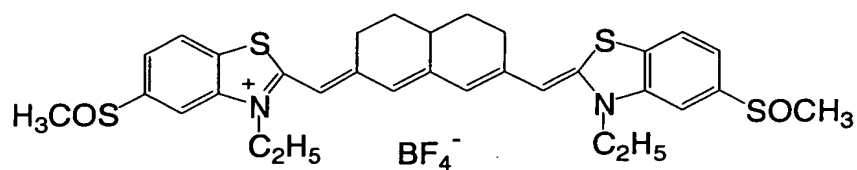
Phthalazine	1.5 g
Tetrachlorophthalic acid	0.5 g
4-Methylphthalic acid	0.5 g
Dye-2	2.0 g
Reducing agent (I-5)	15.0 g
Desmodur N3300 (Mobay, aliphatic isocyanate)	1.10 g
Antifoggant-2	0.9 g

[Formula 23]

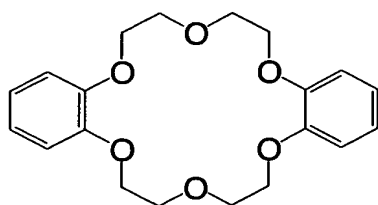
## Polyhalogen Compound-2



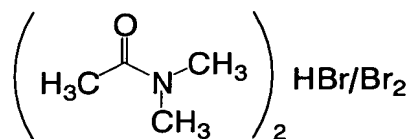
## Sensitizing Dye-3



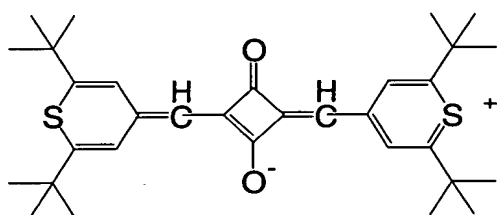
## Dye Adsorption Promoting Agent



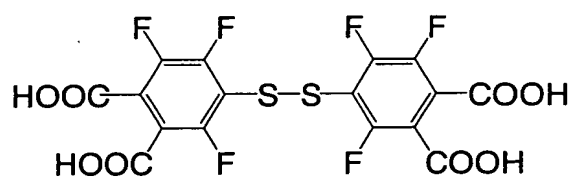
## Antifoggant-1



## Dye-2



## Antifoggant-2



[0233]

3) Coating Solution for Surface Protective Layer

The coating solution for the surface protective layer was prepared in the similar manner to that in Example 1.

4) Coating

Image forming layer: the support had a back layer coated thereon, similarly to that of Example 1. The surface on the reverse side of the back side of this support was simultaneously coated with the coating solution for the image forming layer, so that the coating amount of silver of 1.8 g/m<sup>2</sup> and the amount of polyvinyl butyral in the binder of 8.5 g/m<sup>2</sup> are provided.

Surface protective layer was coated at wet coating amount of 100  $\mu$ m.

[0234]

5) Evaluation of Photographic Performance

Evaluations were carried out in the similar manner to those of Example 1. The results are shown in Table 3.

[0235]

[Table 3]

Photothermo-graphic material	Silver halide emulsion	$\gamma$ value	Result of evaluation	Dmax	Remarks
25	1	5.2	D	4.2	Comparative Example
26	2	4.5	D	3.2	Comparative Example
27	3	4	C	2.2	Present invention
28	1+2 (9:1)	3.7	B	4.1	Present invention
29	1+3 (9:1)	3.2	A	4	Present invention
30	2+3 (9:1)	3.5	B	3.2	Present invention
31	1+2+3 (8:1:1)	3	A	3.9	Present invention
32	upper layer:2 lower layer:1	3.4	B	4.1	Present invention
33	upper layer:3 lower layer:2	3.2	A	3.2	Present invention
34	upper layer:3 lower layer:1	2.9	A	4	Present invention
35	upper layer:2+3 lower layer:1+2	2.8	A	3.9	Present invention
36	upper layer:1+2+3 lower layer:1+2	2.7	A	3.7	Present invention

[0236]

Similarly to Example 1, the developed images having a  $\gamma$  value of 2.0 to 4.0 were uniform in density and exhibited an excellent image quality.

[0237]

Example 5

#### 1) Preparation of Silver Halide Emulsion (Preparation of Silver Halide Emulsion-4)

To 1420 mL of distilled water was added 4.3 mL of a 1% by mass potassium iodide solution. Further, a liquid added with 3.5 mL of sulfuric acid having the concentration of 0.5 mol/L and 36.7 g of phthalated gelatin was kept at 42°C while stirring in a stainless steel reaction pot, and thereto were added total amount of: solution A prepared by diluting 22.22 g of silver nitrate by adding distilled water to give the volume of 195.6 mL; and solution B prepared by diluting 21.8 g of potassium iodide with distilled water to give the volume of 218 mL, over 9 minutes at a constant flow rate. Thereafter, 10 mL of a 3.5% by mass aqueous solution of hydrogen peroxide was added thereto, and 10.8 mL of a 10% by mass aqueous solution of benzimidazole was further added. Moreover, a solution C prepared by diluting 51.86 g of silver nitrate by adding distilled water to give the volume of 317.5 mL and a solution D prepared by diluting 60 g of potassium iodide with distilled water to give the volume of 600 mL were added. A controlled double jet method was executed by adding total amount of the solution C at a constant flow rate over 120 minutes, accompanied by adding the solution D while maintaining the pAg at 8.1.

[0238]

Hexachloroiridium (III) potassium salt was added to give  $1 \times 10^{-4}$  mol per one mol of silver at 10 minutes after initiation of the addition of the solution C and the solution D in its entirety. Moreover, 5 seconds after completing the addition of the solution C, a potassium iron (II) hexacyanide aqueous solution was added in a total amount of  $3 \times 10^{-4}$  mol per one mol of silver. The mixture was adjusted to the pH of 3.8 with sulfuric acid at the concentration of 0.5 mol/L. After stopping stirring, the mixture was subjected to precipitation, desalting and water washing steps. The mixture was adjusted to the pH of 5.9 with sodium hydroxide at the concentration of one mol/L to produce a silver halide dispersion having the pAg of 8.0. Grains in thus prepared silver halide emulsion were pure silver iodide grains having a mean sphere equivalent diameter of 0.030  $\mu\text{m}$ , a variation coefficient of 17%. Grain size and the like were determined from the average of 1000 grains using an electron microscope.

[0239]

The above-mentioned silver halide dispersion was kept at 38°C with stirring, and thereto was added 5 mL of a 0.34% by mass methanol solution of 1,2-benzisothiazoline-3-one, followed by elevating the temperature to 47°C. 20 minutes after elevating the temperature, sodium benzene thiosulfonate in a methanol solution was added in an amount of  $7.6 \times 10^{-5}$  mol per one mol of silver, and then pAg was adjusted to 5.5. Additional 5 minutes later, a tellurium sensitizer C in a methanol solution was added in an amount of  $2.9 \times 10^{-4}$  mol per one mol of silver and subjected to aging for 91 minutes. After adjusting pAg of the emulsion to 7.5, 1.3 mL of a 0.8% by mass N,N'-dihydroxy-N'',N''-diethylmelamine in methanol was added thereto, and additional 4 minutes thereafter, 5-methyl-2-mercaptobenzimidazole in a methanol solution in an amount of  $4.8 \times 10^{-3}$  mol per one mol of silver, 1-phenyl-2-heptyl-5-mercapto-1,3,4-triazole in a methanol solution in an amount of  $5.4 \times 10^{-3}$  mol per one mol of silver were added to produce a silver halide emulsion.

[0240]

#### (Preparation of Silver Halide Emulsion-5 and -6)

Preparation of silver halide emulsion-5 and -6 was conducted in a similar manner to the process in the preparation of the silver halide emulsion-4 except that: the temperature of the liquid upon the nucleation process was altered from 42°C to 50°C or 60°C.

The mean sphere equivalent diameter of the emulsion grains in the silver halide emulsion-5 was 0.050  $\mu\text{m}$ , and that of the grains in the silver halide emulsion-6 was 0.070  $\mu\text{m}$ .

[0241]

2) Preparation of Silver Salt of Fatty Acid

«Preparation of silver salt of fatty acid-8 to -10»

Preparation of silver salts of fatty acid-8 to -10 was conducted in the similar manner to the process in the preparation of silver salt of fatty acid-1 in Example 1, except using silver halide emulsion-4 to -6 instead of using silver halide emulsion-1.

[0242]

«Preparation of silver salt of fatty acid-11 to -14»

Preparation of silver salts of fatty acid-11 to -14 was conducted in the similar manner to the process in the preparation of silver salt of fatty acid-1, except using mixtures of silver halide emulsion-4 to -6 with the rate shown in Table 4 instead of using silver halide emulsion-1.

[0243]

3) Redispersion of Organic Silver Salt in Organic Solvent

Preparation of organic silver salt redispersion-8 to -14 was conducted in the similar manner to the process in the redispersion of organic silver salt in Example 1, except using the above-mentioned silver salts of fatty acid-8 to -14 instead of using silver salts of fatty acid-1 to -7.

[0244]

4) Preparation of Coating Solution for Image Forming Layer-37 to -43

Preparation of coating solution for image forming layer-37 to -43 was conducted in the similar manner to the process in the preparation of coating solution for image forming layer-1 to -7 in Example 1 except that: either of above-mentioned organic silver salt redispersion-8 to -14 was used instead of organic silver salt redispersion-1 to -7, and the sensitizing dye-1 used in the preparation of coating solution for image forming layer-1 to -7 in Example 1 was not added.

[0245]

5) Preparation of Photothermographic Material-37 to -48

Photothermographic material-37 to -43 were prepared by simultaneous double coating of either one of the coating solutions for image forming layer prepared above, and the coating solution for the surface protective layer prepared in Example 1 using a dual knife coater, on a reverse surface to the back layer of the support coated with the back layer. The coating was executed so that the image forming layer had the thickness after drying of 18.3  $\mu\text{m}$ , and that the surface protective layer had the dry film thickness of 3.4  $\mu\text{m}$ . This coating device has two knife coating blades which are laid side by side. After cutting the support to the size so that it meets with the volume of the solution used, knives equipped with a hinge were elevated to put them in a position on the coater floor. Then, the knives were brought down and fixed onto a predetermined position. The height of the knives was regulated using a wedge which was measured with an ammeter and which was controlled by a screw knob. Knife #1 was elevated up to a clearance corresponding to the thickness which was coordinated with total thickness of the substrate thickness and the desired wet thickness of the image forming layer (layer #1). Knife #2 was elevated up to the height equal to the total

thickness of: support thickness + wet thickness of the image forming layer (layer #1) + desired thickness of the surface protective layer (layer #2). Thereafter, drying was performed with an air of the temperature of 75°C and a dew point of 10°C for 15 minutes.

In the case the image forming layer was made of two layers, three knife coating blades were used, and the coating was executed so that the thickness after drying of each of the upper and the lower image forming layer became 9.15  $\mu\text{m}$ . Preparation of photothermographic material-44 to -48 was conducted this way.

#### 6) Exposure and Development

Photothermographic material-37 to -48 were processed in the similar manner to that of Example 1 except using blue laser beam instead of using semiconductor laser which is longitudinally multiple modulated at the wavelength of 800 nm through 820 nm in Example 1. The results are shown in Table 4.

[0246]

[Table 4 ]

Photothermo-graphic material	Silver halide emulsion	$\gamma$ value	Result of evaluation	Dmax	Remarks
37	1	5.3	D	5	Comparative Example
38	2	4.6	D	4	Comparative Example
39	3	4.1	C	3	Present invention
40	1+2 (9:1)	3.8	B	4.9	Present invention
41	1+3 (9:1)	3.2	A	4.8	Present invention
42	2+3 (9:1)	3.6	B	4	Present invention
43	1+2+3 (8:1:1)	3.1	A	4.7	Present invention
44	upper layer:2 lower layer:1	3.5	B	4.9	Present invention
45	upper layer:3 lower layer:2	3.3	B	4.2	Present invention
46	upper layer:3 lower layer:1	3	A	4.8	Present invention
47	upper layer:2+3 lower layer:1+2	2.9	A	4.7	Present invention
48	upper layer:1+2+3 lower layer:1+2	2.8	A	4.5	Present invention

[0247]

As shown in Table 4, in the case silver iodide was used, sensitizing dyes were not added and the images were exposed with a blue laser beam, the developed images having a  $\gamma$  value of 2.0 to 4.0 were uniform in density and exhibited an excellent image quality, similarly to Example 1.

[0248]

#### Example 6

##### 1 Preparation of Coating Solution for Undercoat Layer

Formula (1) (for undercoat layer on the image forming layer side)

Pesresin A-520 manufactured by Takamatsu Oil & Fat Co., Ltd. (30% by mass solution)	59 g
Polyethyleneglycol monononylphenylether (average ethylene oxide number = 8.5) 10% by mass solution	5.4 g
MP-1000 manufactured by Soken Chemical & Engineering Co., Ltd. (polymer fine particle, mean particle diameter of 0.4 $\mu\text{m}$ )	0.91 g
Distilled water	935 mL

[0249]

Formula (2) (for first layer on the back surface)

Styrene-butadiene copolymer latex (solid content of 40% by mass, styrene/butadiene weight ratio = 68/32)	158 g
8% by weight aqueous solution of 2,4-dichloro-6-hydroxy-S-triazine sodium salt	20 g
1% by mass aqueous solution of sodium laurylbenzenesulfonate	10 mL
Distilled water	854 mL

[0250]

Formula (3) (for second layer on the back surface)

$\text{SnO}_2/\text{SbO}$ (9/1 mass ratio, mean particle diameter of 0.038 $\mu\text{m}$ , 17% by mass dispersion)	84 g
Gelatin (10% by mass aqueous solution)	89.2 g
METOLOSE TC-5 manufactured by Shin-Etsu Chemical Co., Ltd. (2% by mass aqueous solution)	8.6 g
MP-1000 manufactured by Soken Chemical & Engineering Co., Ltd.	0.01 g
1% by mass aqueous solution of sodium dodecylbenzenesulfonate	10 mL
NaOH (1% by mass)	6 mL
Proxel (manufactured by Imperial Chemical Industries PLC)	1 mL
Distilled water	805 mL

[0251]

## 2. Undercoating

Both surfaces of the biaxially tented polyethylene terephthalate support having the thickness of 175  $\mu\text{m}$  were subjected to the corona discharge treatment as described above. Thereafter, the aforementioned formula (1) of the coating solution for the undercoat was coated on one surface (image forming layer side) with a wire bar so that the amount of wet coating became 6.6  $\text{mL}/\text{m}^2$  (per one side), and dried at 180°C for 5 minutes. Then, the aforementioned formula (2) of the coating solution for the undercoat was coated on the reverse face (back surface) with a wire bar so that the amount of wet coating became 5.7  $\text{mL}/\text{m}^2$ , and dried at 180°C for 5 minutes. Furthermore, the aforementioned formula (3) of the coating solution for the undercoat was coated on the reverse face (back surface) with a wire bar so that the amount of wet coating became 7.7  $\text{mL}/\text{m}^2$ , and dried at 180°C for 6 minutes. Thus, an undercoated support was produced.



[0252]

3. Preparation of Coating Solution for Back Layer

(Preparation of Dispersion of Solid Fine Particles (a) of Base Precursor)

A base precursor compound-1 in an amount of 2.5 kg, and 300 g of a surfactant (trade name: DEMOL N, manufactured by Kao Corporation), 800 g of diphenyl sulfone, 1.0 g of benzoisothiazolinone sodium salt and distilled water were added to give the total amount of 8.0 kg and mixed. The mixed liquid was subjected to beads dispersion using a horizontal sand mill (UVM-2: manufactured by IMEX Co., Ltd.). Process for dispersion included feeding the mixed liquid to UVM-2 packed with zirconia beads having the mean particle diameter of 0.5 mm with a diaphragm pump, followed by the dispersion at the inner pressure of 50 hPa or higher until desired mean particle diameter could be achieved.

The dispersion was continued until the ratio of the optical density at 450 nm and the optical density at 650 nm for the spectral absorption of the dispersion (D450/ D650) became 3.0 upon spectral absorption measurement. Thus resulting dispersion was diluted with distilled water so that the concentration of the base precursor became 25% by weight, filtrated (with a polypropylene filter having the mean fine pore diameter of 3  $\mu$ m) for eliminating dust, and was put into practical use.

[0253]

4. Preparation of Coating Solution for Antihalation Layer

(Preparation of Dispersion of Solid Fine Particle of Dye)

A cyanine dye compound-1 in an amount of 6.0 kg, and 3.0 kg of sodium p-dodecylbenzenesulfonate, 0.6 kg of DEMOL SNB (a surfactant manufactured by Kao Corporation), and 0.15 kg of a defoaming agent (trade name: SURFYNOL 104E, manufactured by Nissin Chemical Industry Co., Ltd.) were mixed with distilled water to give the total liquid amount of 60 kg. The mixed liquid was subjected to dispersion with 0.5 mm zirconia beads using a horizontal sand mill (UVM-2: manufactured by IMEX Co., Ltd.).

The dispersion was dispersed until the ratio of the optical density at 650 nm and the optical density at 750 nm for the spectral absorption of the dispersion (D650/ D750) became 5.0 or greater upon spectral absorption measurement. Thus resulting dispersion was diluted with distilled water so that the concentration of the cyanine dye became 6% by mass, filtrated with a filter (mean fine pore diameter: 1  $\mu$ m) for eliminating dust, and was put into practical use.

[0254]

(Preparation of Coating Solution for Antihalation Layer)

A vessel was kept at 40°C, and thereto were added 40 g of gelatin, 20 g of monodispersed polymethyl methacrylate fine particles (mean particle size of 8  $\mu$ m, standard deviation of particle diameter of 0.4), 0.1 g of benzoisothiazolinone and 490 mL of water to allow gelatin to be dissolved. Additionally, 2.3 mL of a 1 mol/L aqueous sodium hydroxide solution, 40 g of the aforementioned dispersion of the solid fine particle of the dye, 90 g of the aforementioned dispersion of the solid fine particles (a) of the base precursor, 12 mL of a 3% by weight aqueous solution of sodium polystyrenesulfonate, and 180 g of a 10% by weight solution of SBR latex were admixed. Just prior to the coating, 80 mL of a 4% by weight aqueous solution of N,N-ethylenebis(vinylsulfone acetamide) was admixed to give a coating solution for the antihalation layer.

[0255]

5. Preparation of Coating Solution for Back Surface Protective Layer

A vessel was kept at 40°C, and thereto were added 40 g of gelatin, 35 mg of

benzothiazolinone and 840 ml of water to allow gelatin to be dissolved. Additionally, 5.8 ml of a 1 mol/L aqueous sodium hydroxide solution, liquid paraffin emulsion at 1.5 g equivalent to liquid paraffin, 10 mL of a 5% by weight aqueous solution of di(2-ethylhexyl) sodium sulfosuccinate, 20 mL of a 3% by weight aqueous solution of sodium polystyrenesulfonate, 2.4 mL of a 2% by weight solution of a fluorochemical surfactant (F-1), 2.4 mL of a 2% by weight solution of a fluorocarbon surfactant (F-2), and 32 g of a 19% by mass solution of methyl methacrylate/ styrene/ butyl acrylate/ hydroxyethyl methacrylate/ acrylic acid copolymer (copolymer weight ratio of 57/8/28/5/2) latex were admixed. Just prior to the coating, 25 mL of a 4% by weight aqueous solution of N,N-ethylenebis(vinylsulfone acetamide) was admixed to give a coating solution for the back surface protective layer.

[0256]

#### 6. Coating of Back Layer

The back surface side of the undercoated support as described above was subjected to simultaneous double coating so that the coating solution for the antihalation layer gives the coating amount of gelatin of 0.52 g/m<sup>2</sup>, and so that the coating solution for the back surface protective layer gives the coating amount of gelatin of 1.7 g/m<sup>2</sup>, followed by drying to produce a back layer.

[0257]

#### 7. Preparation of Image Forming Layer, Intermediate Layer, and Surface Protective Layer

##### 1) Preparation of Materials for Coating

##### (Silver Halide Emulsion)

##### <<Preparation of Silver Halide Emulsion-7>>

To 1421 mL of distilled water was added 3.1 mL of a 1% by mass potassium bromide solution. Further, a liquid added with 3.5 mL of sulfuric acid having the concentration of 0.5 mol/L and 31.7 g of phthalated gelatin was kept at 30°C while stirring in a stainless steel reaction pot, and thereto were added total amount of: solution A prepared through diluting 22.22 g of silver nitrate by adding distilled water to give the volume of 95.4 mL; and solution B prepared through diluting 15.3 g of potassium bromide and 0.8 g of potassium iodide with distilled water to give the volume of 97.4 mL, over 45 seconds at a constant flow rate. Thereafter, 10 mL of a 3.5% by mass aqueous solution of hydrogen peroxide was added thereto, and 10.8 mL of a 10% by mass aqueous solution of benzimidazole was further added. Moreover, a solution C prepared through diluting 51.86 g of silver nitrate by adding distilled water to give the volume of 317.5 mL and a solution D prepared through diluting 44.2 g of potassium bromide and 2.2 g of potassium iodide with distilled water to give the volume of 400 mL were added. A controlled double jet method was executed through adding total amount of the solution C at a constant flow rate over 20 minutes, accompanied by adding the solution D while maintaining the pAg at 8.1. Hexachloroiridium (III) potassium salt was added to give  $1 \times 10^{-4}$  mol per one mol of silver at 10 minutes post initiation of the addition of the solution C and the solution D in its entirety. Moreover, at 5 seconds after completing the addition of the solution C, a potassium iron (II) hexacyanide aqueous solution was added at a total amount of  $3 \times 10^{-4}$  mol per one mol of silver. The mixture was adjusted to the pH of 3.8 with sulfuric acid at the concentration of 0.5 mol/L. After stopping stirring, the mixture was subjected to precipitation/ desalting/ water washing steps. The mixture was adjusted to the pH of 5.9 with sodium hydroxide at the concentration of one mol/L to produce a silver halide dispersion having the pAg of 8.0.

[0258]

The silver halide dispersion was kept at 38°C with stirring, and thereto was added 5 mL of a 0.34% by mass methanol solution of 1,2-benzisothiazoline-3-one, followed by elevating the temperature to 47°C at 40 minutes thereafter. 20 minutes after elevating the temperature, sodium benzene thiosulfonate in a methanol solution was added in an amount of  $7.6 \times 10^{-5}$  mol per one mol of silver. Additional 5 minutes later, a tellurium sensitizer C in a methanol solution was added in an amount of  $2.9 \times 10^{-4}$  mol per one mol of silver and subjected to aging for 91 minutes. Thereafter, a methanol solution of a spectral sensitizer A and a spectral sensitizer B with a molar ratio of 3 : 1 was added thereto in an amount of  $1.2 \times 10^{-3}$  mol in total of the spectral sensitizer A and B per one mol of silver. One minute later, 1.3 mL of a 0.8% by mass N,N'-dihydroxy-N'',N''-diethylmelamine in methanol was added thereto, and additional 4 minutes thereafter, 5-methyl-2-mercaptobenzimidazole in a methanol solution in an amount of  $4.8 \times 10^{-3}$  mol per one mol of silver, 1-phenyl-2-heptyl-5-mercapto-1,3,4-triazole in a methanol solution in an amount of  $5.4 \times 10^{-3}$  mol per one mol of silver, and 1-(3-methylureidophenyl)-5-mercaptotetrazole in an aqueous solution in an amount of  $8.5 \times 10^{-3}$  mol per one mol of silver were added to produce a silver halide emulsion-7.

[0259]

Grains in thus prepared silver halide emulsion were silver iodide bromide grains having a mean sphere equivalent diameter of 0.042  $\mu\text{m}$ , a variation coefficient of 20%, which uniformly include iodine in an amount of 3.5 mol%. Grain size and the like were determined from the average of 1000 grains using an electron microscope. The [100] face ratio of these grains were found to be 80% using a Kubelka-Munk method.

[0260]

<<Preparation of Silver Halide Emulsion-8>>

Preparation of silver halide emulsion-2 was conducted in a similar manner to the process in the preparation of the silver halide emulsion-7 except that: the temperature of the liquid upon the nucleation process was altered from 30°C to 47°C; the solution B was changed to that prepared by diluting 15.9 g of potassium bromide with distilled water to give the volume of 97.4 mL; the solution D was changed to that prepared by diluting 45.8 g of potassium bromide with distilled water to give the volume of 400 mL; time period for adding the solution C was changed to 30 minutes; and potassium iron (II) hexacyanide was deleted. The precipitation/ desalting/ water washing /dispersion were carried out similarly to the silver halide emulsion-1. Furthermore, the spectral sensitization, chemical sensitization, and addition of 5-methyl-2-mercaptobenzimidazole and 1-phenyl-2-heptyl-5-mercapto-1,3,4-triazole was executed similarly to the emulsion-1 except that: the amount of the tellurium sensitizer C to be added was changed to  $1.1 \times 10^{-4}$  mol per one mol of silver; the amount of the methanol solution of the spectral sensitizer A and a spectral sensitizer B with a molar ratio of 3 : 1 to be added was changed to  $7.0 \times 10^{-4}$  mol in total of the spectral sensitizer A and the spectral sensitizer B per one mol of silver; the addition of 1-phenyl-2-heptyl-5-mercapto-1,3,4-triazole was changed to give  $3.3 \times 10^{-3}$  mol per one mol of silver; and the addition of 1-(3-methylureidophenyl)-5-mercaptotetrazole was changed to give  $4.7 \times 10^{-3}$  mol per one mol of silver to produce a silver halide emulsion-8. The emulsion grains in the silver halide emulsion-8 were pure cubic silver bromide grains having a mean sphere equivalent diameter of 0.080  $\mu\text{m}$  and a variation coefficient of 20%.

[0261]

<<Preparation of Silver Halide Emulsion-9>>

Preparation of a silver halide emulsion-3 was conducted in a similar manner to the process in the preparation of the silver halide emulsion-7 except that the temperature of the

liquid upon the nucleation process was altered from 30°C to 27°C. In addition, the precipitation/ desalting/ water washing /dispersion were carried out similarly to the silver halide emulsion-1. Silver halide emulsion-9 was obtained similarly to the emulsion-1 except that: the addition of the methanol solution of the spectral sensitizer A and the spectral sensitizer B was changed to the solid dispersion (aqueous gelatin solution) at a molar ratio of 1 : 1 with the amount to be added being  $6.0 \times 10^{-3}$  mol in total of the spectral sensitizer A and spectral sensitizer B per one mol of silver; the amount of the tellurium sensitizer C to be added was changed to  $5.2 \times 10^{-4}$  mol per one mol of silver; and bromoauric acid at  $5 \times 10^{-4}$  mol per one mol of silver and potassium thiocyanate at  $2 \times 10^{-3}$  mol per one mol of silver were added 3 minutes after the addition of the tellurium sensitizer. The grains in the silver halide emulsion-9 were silver iodide bromide grains having a mean sphere equivalent diameter of 0.034  $\mu\text{m}$  and a variation coefficient of 20%, which uniformly include iodine at 3.5 mol%.

[0262]

<<Preparation of Mixed Emulsion A for Coating Solution>>

The silver halide emulsion-1 in an amount of 70% by mass, the silver halide emulsion-2 in an amount of 15% by mass and the silver halide emulsion-3 in an amount of 15% by mass were dissolved, and thereto was added benzothiazolium iodide in an amount of  $7 \times 10^{-3}$  mol per one mol of silver with a 1% by mass aqueous solution. Further, water was added thereto to give the content of silver of 38.2 g per one kg of the mixed emulsion for a coating solution, and 1-(3-methylureidophenyl)-5-mercaptotetrazole was added to give 0.34 g per 1 kg of the mixed emulsion for a coating solution.

[0263]

(Preparation of Dispersion of Silver Salt of Fatty Acid)

<<Preparation of Dispersion of Silver Salt of Fatty Acid B>>

<Preparation of recrystallized behenic acid>

100 kg of behenic acid (Henkel Co., trade name: Edenor C22-85R) was mixed with 1200 kg of isopropyl alcohol and dissolved at 50°C. The resulting mixture was filtered with a filter having a pore size of 10  $\mu\text{m}$  and was cooled for recrystallization. The cooling speed at the time of recrystallization was controlled to be 3°C/hour. Crystals obtained were subjected to centrifugal filtration, washing with 100 kg of isopropyl alcohol and drying. The crystals were esterified and subjected to GC-FID measurement. The crystals contained 96% of behenic acid, 2% of lignoceric acid, 2% of arachidic acid and 0.001% of erucic acid.

[0264]

<Preparation of Dispersion of Silver Salt of Fatty Acid B>

88 kg of the recrystallized behenic acid, 422 L of distilled water, 49.2 L of an aqueous NaOH solution at the concentration of 5 mol/L, 120 L of t-butyl alcohol were admixed, and subjected to a reaction with stirring at 75°C for one hour to give a solution B of sodium behenate. Separately, 206.2 L of an aqueous solution of 40.4 kg of silver nitrate (pH 4.0) was provided, and kept at a temperature of 10°C. A reaction vessel charged with 635 L of distilled water and 30 L of t-butyl alcohol was kept at 30°C, and thereto were added the total amount of the solution B of sodium behenate and the total amount of the aqueous silver nitrate solution with sufficient stirring at a constant flow rate over 93 minutes and 15 seconds, and 90 minutes, respectively. Upon this operation, during first 11 minutes following the initiation of adding the aqueous silver nitrate solution, the added material was restricted to the aqueous silver nitrate solution alone. The addition of the solution B of sodium behenate was thereafter started, and during 14 minutes and 15 seconds following the completion of adding the aqueous silver nitrate solution, the added material was restricted to the solution B of

sodium behenate alone. The temperature inside of the reaction vessel was then set to be 30°C, and the temperature outside was controlled so that the liquid temperature could be kept constant. In addition, the temperature of a pipeline for the addition system of the solution B of sodium behenate was kept constant by circulation of warm water outside of a double wall pipe, so that the temperature of the liquid at an outlet in the leading edge of the nozzle for addition was adjusted to be 75°C. Further, the temperature of a pipeline for the addition system of the aqueous silver nitrate solution was kept constant by circulation of cool water outside of a double wall pipe. Position at which the solution B of sodium behenate was added and the position at which the aqueous silver nitrate solution was added were arranged symmetrically with a shaft for stirring located at a center. Moreover, both of the positions were adjusted to avoid contact with the reaction liquid.

[0265]

After completing the addition of the solution B of sodium behenate, the mixture was left to stand at the temperature as it was for 20 minutes. The temperature of the mixture was then elevated to 35°C over 30 minutes followed by aging for 210 minutes. Immediately after completing the aging, solid matters were filtered out with centrifugal filtration. The solid matters were washed with water until the electric conductivity of the filtrated water became 30 µS/cm. A silver salt of the fatty acids was thus obtained. The resulting solid matters were stored as a wet cake without drying.

When the shape of the resulting particles of the silver behenate was evaluated by an electron micrography, it was revealed that a flake crystal had the following:  $a = 0.21\text{ }\mu\text{m}$ ,  $b = 0.4\text{ }\mu\text{m}$  and  $c = 0.4\text{ }\mu\text{m}$  on the average value, a mean aspect ratio of 2.1 and a variation coefficient of 11% ( $a$ ,  $b$  and  $c$  are as defined aforementioned).

[0266]

To the wet cake corresponding to 260 kg of a dry solid matter content, were added 19.3 kg of polyvinyl alcohol (trade name: PVA-217) and water to give the total amount of 1000 kg. Then, slurry was obtained from the mixture using a dissolver blade. Additionally, the slurry was subjected to preliminary dispersion with a pipeline mixer (manufactured by MIZUHO Industrial Co., Ltd.: PM-10 type).

[0267]

Next, a stock liquid after the preliminary dispersion was treated three times using a dispersing machine (trade name: Microfluidizer M-610, manufactured by Microfluidex International Corporation, using Z type Interaction Chamber) with the pressure controlled to be 1150 kg/cm<sup>2</sup> to give a dispersion of the silver behenate. For the cooling manipulation, coiled heat exchangers were provided at the front and the rear of the interaction chamber, and accordingly, the temperature for the dispersion was set to be 18°C by regulating the temperature of the cooling medium.

[0268]

(Preparation of Reducing Agent Dispersion)

<<Preparation of Reducing Agent-1 Dispersion>>

To 10 kg of a reducing agent-1 (2,2'-methylenebis(4-ethyl-6-tert-butylphenol)) and 16 kg of a 10% by mass aqueous solution of modified polyvinyl alcohol (manufactured by Kuraray Co., Ltd., Poval MP203) was added 10 kg of water, and thoroughly mixed to give slurry. This slurry was fed with a diaphragm pump, and was subjected to dispersion with a horizontal sand mill (UVM-2: manufactured by IMEX Co., Ltd.) packed with zirconia beads having the mean particle diameter of 0.5 mm for 3 hours. Thereafter, 0.2 g of a

benzothiazolinone sodium salt and water were added thereto, thereby adjusting the concentration of the reducing agent to be 25% by mass. This dispersion was subjected to thermal treatment at 60°C for 5 hours to obtain a reducing agent-1 dispersion. Particles of the reducing agent included in thus resulting reducing agent dispersion had a median diameter of 0.40 µm, and a maximum particle diameter of 1.4 µm or less. The resultant reducing agent dispersion was subjected to filtration with a polypropylene filter having a pore size of 3.0 µm to remove foreign substances such as dust, and was stored.

[0269]

<<Preparation of Reducing Agent-2 Dispersion>>

To 10 kg of a reducing agent-2 (6,6'-di-*t*-butyl-4,4'-dimethyl-2,2'-butylidenediphenol)) and 16 kg of a 10% by mass aqueous solution of modified polyvinyl alcohol (manufactured by Kuraray Co., Ltd., Poval MP203) was added 10 kg of water, and thoroughly mixed to give slurry. This slurry was fed with a diaphragm pump, and was subjected to dispersion with a horizontal sand mill (UVM-2: manufactured by IMEX Co., Ltd.) packed with zirconia beads having the mean particle diameter of 0.5 mm for 3 hours and 30 minutes. Thereafter, 0.2 g of a benzothiazolinone sodium salt and water were added thereto, thereby adjusting the concentration of the reducing agent to be 25% by mass. This dispersion was warmed at 40°C for one hour, followed by a subsequent thermal treatment at 80°C for one hour to obtain a reducing agent-2 dispersion. Particles of the reducing agent included in thus resulting reducing agent-2 dispersion had a median diameter of 0.50 µm, and a maximum particle diameter of 1.6 µm or less. The resultant reducing agent-2 dispersion was subjected to filtration with a polypropylene filter having a pore size of 3.0 µm to remove foreign substances such as dust, and was stored.

[0270]

(Preparation of Hydrogen Bonding Compound Dispersion)

To 10 kg of a hydrogen bonding compound-1 (tri(4-*t*-butylphenyl)phosphineoxide) and 16 kg of a 10% by mass aqueous solution of modified polyvinyl alcohol (manufactured by Kuraray Co., Ltd., Poval MP203) was added 10 kg of water, and thoroughly mixed to give slurry. This slurry was fed with a diaphragm pump, and was subjected to dispersion with a horizontal sand mill (UVM-2: manufactured by IMEX Co., Ltd.) packed with zirconia beads having the mean particle diameter of 0.5 mm for 4 hours. Thereafter, 0.2 g of a benzothiazolinone sodium salt and water were added thereto, thereby adjusting the concentration of the hydrogen bonding compound to be 25% by mass. This dispersion was warmed at 40°C for one hour, followed by a subsequent thermal treatment at 80°C for one hour to obtain a hydrogen bonding compound dispersion. Particles of the hydrogen bonding compound included in thus resulting hydrogen bonding compound-1 dispersion had a median diameter of 0.45 µm, and a maximum particle diameter of 1.3 µm or less. The resultant hydrogen bonding compound-1 dispersion was subjected to filtration with a polypropylene filter having a pore size of 3.0 µm to remove foreign substances such as dust, and was stored.

[0271]

(Preparation of Development Accelerator-1 Dispersion)

To 10 kg of a development accelerator-1 and 20 kg of a 10% by mass aqueous solution of modified polyvinyl alcohol (manufactured by Kuraray Co., Ltd., Poval MP203) was added 10 kg of water, and thoroughly mixed to give slurry. This slurry was fed with a diaphragm pump, and was subjected to dispersion with a horizontal sand mill (UVM-2: manufactured by IMEX Co., Ltd.) packed with zirconia beads having the mean particle diameter of 0.5 mm for 3 hours and 30 minutes. Thereafter, 0.2 g of a benzothiazolinone

sodium salt and water were added thereto, thereby adjusting the concentration of the development accelerating agent to be 20% by mass. Accordingly, a development accelerator-1 dispersion was obtained. Particles of the development accelerator included in thus resulting development accelerator dispersion had a median diameter of 0.48  $\mu\text{m}$ , and a maximum particle diameter of 1.4  $\mu\text{m}$  or less. The resultant development accelerator dispersion was subjected to filtration with a polypropylene filter having a pore size of 3.0  $\mu\text{m}$  to remove foreign substances such as dust, and was stored.

Also concerning solid dispersions of a development accelerator-2 and a color-tone-adjusting agent-1, dispersion was executed in a similar manner to that of the development accelerator-1, and thus dispersions of 20% by mass and 15% by mass were respectively obtained.

[0272]

(Preparation of Polyhalogen Compound)

<<Preparation of Organic Polyhalogen Compound-1 Dispersion>>

An organic polyhalogen compound-1 (tribromomethane sulfonylbenzene) in an amount of 10 kg, 10 kg of a 20% by mass aqueous solution of modified polyvinyl alcohol (manufactured by Kuraray Co., Ltd., Poval MP203), 0.4 kg of a 20% by mass aqueous solution of sodium triisopropylphenylsulfonate and 14 kg of water were added, and thoroughly admixed to give slurry. This slurry was fed with a diaphragm pump, and was subjected to dispersion with a horizontal sand mill (UVM-2: manufactured by IMEX Co., Ltd.) packed with zirconia beads having the mean particle diameter of 0.5 mm for 5 hours. Thereafter, 0.2 g of a benzoisothiazolinone sodium salt and water were added thereto, thereby adjusting the concentration of the organic polyhalogen compound to be 26% by mass. Accordingly, an organic polyhalogen compound-1 dispersion was obtained. Particles of the organic polyhalogen compound included in thus resulting polyhalogen compound dispersion had a median diameter of 0.41  $\mu\text{m}$ , and a maximum particle diameter of 2.0  $\mu\text{m}$  or less. The resultant organic polyhalogen compound dispersion was subjected to filtration with a polypropylene filter having a pore size of 10.0  $\mu\text{m}$  to remove foreign substances such as dust, and was stored.

[0273]

<<Preparation of Organic Polyhalogen Compound-2 Dispersion>>

An organic polyhalogen compound-2 (N-butyl-3-tribromomethane sulfonylbenzoamide) in an amount of 10 kg, 20 kg of a 10% by mass aqueous solution of modified polyvinyl alcohol (manufactured by Kuraray Co., Ltd., Poval MP203) and 0.4 kg of a 20% by mass aqueous solution of sodium triisopropylphenylsulfonate were added, and thoroughly admixed to give slurry. This slurry was fed with a diaphragm pump, and was subjected to dispersion with a horizontal sand mill (UVM-2: manufactured by IMEX Co., Ltd.) packed with zirconia beads having the mean particle diameter of 0.5 mm for 5 hours. Thereafter, 0.2 g of a benzoisothiazolinone sodium salt and water were added thereto, thereby adjusting the concentration of the organic polyhalogen compound to be 30% by mass. This fluid dispersion was heated at 40°C for 5 hours to obtain an organic polyhalogen compound-2 dispersion. Particles of the organic polyhalogen compound included in thus resulting polyhalogen compound dispersion had a median diameter of 0.40  $\mu\text{m}$ , and a maximum particle diameter of 1.3  $\mu\text{m}$  or less. The resultant organic polyhalogen compound dispersion was subjected to filtration with a polypropylene filter having a pore size of 3.0  $\mu\text{m}$  to remove foreign substances such as dust, and was stored.

[0274]

(Preparation of Phthalazine Compound-1 Solution)

Modified polyvinyl alcohol MP203 manufactured by Kuraray Co., Ltd., in an amount of 8 kg was dissolved in 174.57 kg of water, and then thereto were added 3.15 kg of a 20% by mass aqueous solution of sodium triisopropylphthalenesulfonate and 14.28 kg of a 70% by mass aqueous solution of a phthalazine compound-1 (6-isopropyl phthalazine) to prepare a 5% by mass phthalazine compound-1 solution.

[0275]

(Preparation of Mercapto Compound)

<<Preparation of an Aqueous Solution of Mercapto Compound-1 >>

A mercapto compound-1 (1-(3-sulfophenyl)-5-mercaptotetrazole sodium salt) in an amount of 7 g was dissolved in 993 g of water to give a 0.7% by mass aqueous solution.

[0276]

<<Preparation of an Aqueous Solution of Mercapto Compound-2 >>

A mercapto compound-2 (1-(3-methylureidophenyl)-5-mercaptotetrazole) in an amount of 20 g was dissolved in 980 g of water to give a 2.0% by mass aqueous solution.

[0277]

(Preparation of Pigment-1 Dispersion)

C.I. Pigment Blue 60 in an amount of 64 g and 6.4 g of DEMOL N manufactured by Kao Corporation were added to 250 g water and thoroughly mixed to give slurry. Zirconia beads having the mean particle diameter of 0.5 mm were provided in an amount of 800 g, and charged in a vessel with the slurry. Dispersion was performed with a dispersing machine (1/4G sand grinder mill: manufactured by IMEX Co., Ltd.) for 25 hours. Thereto was added water to adjust so that the concentration of the pigment became 5% by mass to obtain a pigment-1 dispersion. Particles of the pigment included in thus resulting pigment dispersion had a mean particle diameter of 0.21  $\mu\text{m}$ .

[0278]

(Preparation of SBR Latex Solution)

SBR latex was prepared as described below.

To a polymerization tank of a gas monomer reaction apparatus (manufactured by Taiatsu Techno Corporation, TAS-2J type), were charged 287 g of distilled water, 7.73 g of a surfactant (Pionin A-43-S (manufactured by TAKEMOTO OIL & FAT CO., LTD.): solid matter content of 48.5% by weight), 14.06 mL of 1 mol/liter NaOH, 0.15 g of ethylenediamine tetraacetate tetrasodium salt, 255 g of styrene, 11.25 g of acrylic acid, and 3.0 g of tert-dodecyl mercaptan, followed by sealing of the reaction vessel and stirring at a stirring rate of 200 rpm. Degassing was conducted with a vacuum pump, followed by repeating nitrogen gas replacement several times. Thereinto was injected 108.75 g of 1,3-butadiene, and the inner temperature was elevated to 60°C. Thereto was added a solution of 1.875 g of ammonium persulfate dissolved in 50 mL of water, and the mixture was stirred for 5 hours as it stood. The temperature was further elevated to 90°C, followed by stirring for 3 hours. After completing the reaction, the inner temperature was lowered to reach the room temperature, and thereafter the mixture was treated by adding 1 mol/liter NaOH and  $\text{NH}_4\text{OH}$  to give the molar ration of  $\text{Na}^+$  ion :  $\text{NH}_4^+$  ion = 1 : 5.3, and thus, the pH of the mixture was adjusted to 8.4. Thereafter, filtration with a polypropylene filter having the pore size of 1.0  $\mu\text{m}$  was conducted to remove foreign substances such as dust followed by storage. Accordingly, SBR latex was obtained in an amount of 774.7 g. Upon the measurement of halogen ion by ion chromatography, concentration of chloride ion was revealed to be 3 ppm.



As a result of the measurement of the concentration of the chelating agent by high performance liquid chromatography, it was revealed to be 145 ppm.

[0279]

The aforementioned latex had the mean particle diameter of 90 nm, Tg of 17°C, solid matter concentration of 44% by mass, the equilibrium moisture content at 25°C, 60% RH of 0.6% by mass, ionic conductance of 4.80 mS/cm (measurement of the ionic conductance performed using a conductivity meter CM-30S manufactured by Toa Electronics Ltd. for the latex stock solution (44% by mass) at 25°C).

[0280]

(Preparation of Coating Solution for Image Forming Layer-49)

The dispersion B of the silver salt of fatty acid obtained as described above in an amount of 1000 g, 135 mL of water, 36 g of the pigment-1 dispersion, 25 g of the organic polyhalogen compound-1 dispersion, 39 g of the organic polyhalogen compound-2 dispersion, 171 g of the phthalazine compound-1 solution, 1060 g of the SBR latex (Tg: 17°C) solution, 153 g of the reducing agent-2 dispersion, 55 g of the hydrogen bonding compound-1 dispersion, 4.8 g of the development accelerator-1 dispersion, 5.2 g of the development accelerator-2 dispersion, 2.1 g of the color-tone-adjusting agent-1 dispersion, and 8 mL of the mercapto compound-2 aqueous solution were serially added. The coating solution for the image forming layer prepared by adding 140 g of the silver halide emulsion 7 for a coating solution thereto followed by thorough mixing just prior to the coating was fed directly to a coating die, and was coated.

[0281]

Viscosity of the coating solution for the image forming layer was measured with a B type viscometer from Tokyo Keiki, and was revealed to be 40 [mPa·s] at 40°C (No. 1 rotor, 60 rpm).

Viscosity of the coating solution at 38°C when it was measured using RheoStress RS150 manufactured by Haake was 30, 43, 41, 28, and 20 [mPa·s] at the shearing rates of 0.1, 1, 10, 100, 1000 [1/second], respectively.

[0282]

(Preparation of Coating Solutions for Image Forming Layer-50 to -55)

Coating solutions for image forming layer-50 to -55 were prepared in the same way as in the preparation of the coating solution for image forming layer-49, except that the silver halide emulsions 8 to 13 for a coating solution were used instead of the silver halide emulsion 7.

[0283]

The amount of zirconium in the coating solution was 0.32 mg per one g of silver.

[0284]

(Preparation of Coating Solution for Emulsion Surface-Side Intermediate Layer)

To 1000 g of polyvinyl alcohol PVA-205 (manufactured by Kuraray Co., Ltd.), 163 g of the pigment-1 dispersion, 33g of an aqueous solution of a blue dye-1 (manufactured by Nippon Kayaku Co., Ltd.: Kayafect turquoise RN liquid 150), 27 mL of a 5% by mass aqueous solution of di(2-ethylhexyl) sodium sulfosuccinate and 4200 mL of a 19% by mass solution of methyl methacrylate/ styrene/ butyl acrylate/ hydroxyethyl methacrylate/ acrylic acid copolymer (weight ratio of the copolymerization of 57/ 8/ 28/ 5/ 2) latex, were added 27

mL of a 5% by mass aqueous solution of aerosol OT (manufactured by American Cyanamid Co.), 135 mL of a 20% by mass aqueous solution of ammonium secondary phthalate and water to give total amount of 10000 g. The mixture was adjusted with NaOH to give the pH of 7.5. Accordingly, the coating solution for the intermediate layer was prepared, and was fed to a coating die to provide 8.9 mL/m<sup>2</sup>.

Viscosity of the coating solution was 58 [mPa's] which was measured with a B type viscometer at 40°C (No. 1 rotor, 60 rpm).

[0285]

#### 9. Preparation of Coating Solution for First Layer of Emulsion Surface-Side Surface Protective Layers

In 840 mL of water were dissolved 100 g of inert gelatin and 10 mg of benzoisothiazolinone, and thereto were added 180 g of a 19% by mass solution of methyl methacrylate/ styrene/ butyl acrylate/ hydroxyethyl methacrylate/ acrylic acid copolymer (weight ratio of the copolymerization of 57/ 8/ 28/ 5/ 2) latex, 46 mL of a 15% by mass methanol solution of phthalic acid and 5.4 mL of a 5% by mass aqueous solution of di(2-ethylhexyl) sodium sulfosuccinate, and were mixed. Immediately before coating, 40 mL of a 4% by mass chrome alum which had been mixed with a static mixer was fed to a coating die so that the amount of the coating solution became 26.1 mL/m<sup>2</sup>.

Viscosity of the coating solution was 20 [mPa's] which was measured with a B type viscometer at 40°C (No. 1 rotor, 60 rpm).

[0286]

#### 10. Preparation of Coating Solution for Second Layer of Emulsion Surface-Side Surface Protective Layers

In 800 mL of water were dissolved 100 g of inert gelatin and 10 mg of benzoisothiazolinone, and thereto were added 180 g of a 19% by mass solution of methyl methacrylate/ styrene/ butyl acrylate/ hydroxyethyl methacrylate/ acrylic acid copolymer (weight ratio of the copolymerization of 57/ 8/ 28/ 5/ 2) latex, 40 mL of a 15% by mass methanol solution of phthalic acid, 5.5 mL of a 1% by mass solution of a fluorocarbon surfactant (F-1), 5.5 mL of a 1% by mass aqueous solution of a fluorocarbon surfactant (F-2), 28 mL of a 5% by mass aqueous solution of di(2-ethylhexyl) sodium sulfosuccinate, 4 g of polymethyl methacrylate fine particles (mean particle diameter of 0.7 µm) and 21 g of polymethyl methacrylate fine particles (mean particle diameter of 4.5 µm), and were mixed to give a coating solution for the surface protective layer, which was fed to a coating die so that 8.3 mL/m<sup>2</sup> could be provided.

Viscosity of the coating solution was 19 [mPa's] which was measured with a B type viscometer at 40°C (No. 1 rotor, 60 rpm).

[0287]

#### 11. Preparation of Photothermographic Materials-49 to -60

The back surface side of the undercoated support was subjected to simultaneous double coating so that the coating solution for the antihalation layer gives the coating amount of gelatin of 0.52 g/m<sup>2</sup>, and so that the coating solution for the back surface protective layer gives the coating amount of gelatin of 1.7 g/m<sup>2</sup>, followed by drying to produce a back layer.

[0288]

Reverse surface of the back surface was subjected to simultaneous overlaying coating by a slide bead coating method in order of each of the image forming layers 49 to 55, intermediate layer, first layer of the protective layer and second layer of the protective layer

starting from the undercoated face, and thus the photothermographic materials-49 to -55 were produced. In this method, the temperature of the coating solution was adjusted to 31°C for the image forming layer and intermediate layer, to 36°C for the first layer of the protective layer, and to 37°C for the second layer of the protective layer.

Further, in the photothermographic materials-56 to -60, the image forming layers comprising two layers in the combinations given in Table 5 were coated as the second layers.

The coating amount of each compound for the image forming layer (g/m<sup>2</sup>) is as follows.

[0289]

Silver behenate	5.27
Pigment (C. I. Pigment Blue 60)	0.036
Polyhalogen compound-1	0.14
Polyhalogen compound 2	0.28
Phthalazine compound-1	0.18
SBR latex	9.43
Reducing agent-2	0.77
Hydrogen bonding compound-1	0.28
Development accelerator-1	0.019
Development accelerator-2	0.016
Color-tone-adjusting agent-1	0.006
Mercapto compound-2	0.003
Silver halide (on the basis of Ag content)	0.13

[0290]

Conditions for coating and drying are as follows.

Coating was performed at the speed of 160 m/min, with the clearance between the leading end of the coating die and the support being 0.10 mm to 0.30 mm, and with the pressure in the vacuum chamber set to be lower than atmospheric pressure by 196 Pa to 882 Pa. The support was decharged by ionic wind prior to coating.

In the subsequent cooling zone, the coating solution was cooled by wind having the dry-bulb temperature of 10 °C to 20°C. Thereafter, conveyance with no contact was carried out, and the coated support was dried with an air of the dry-bulb of 23 °C to 45°C and the wet-bulb of 15 °C to 21°C in a helical type contactless drying apparatus.

After drying, moisture conditioning was performed at 25°C in the humidity of 40% RH to 60% RH. Then, the film surface was heated to be 70°C to 90°C. After heating, the film surface was cooled to 25°C.

Thus prepared photothermographic material had the matness of 550 seconds on the image forming layer side surface, and 130 seconds on the back surface as Beck's smoothness. In addition, measurement of the pH of the film surface on the image forming layer side surface gave the result of 6.0.

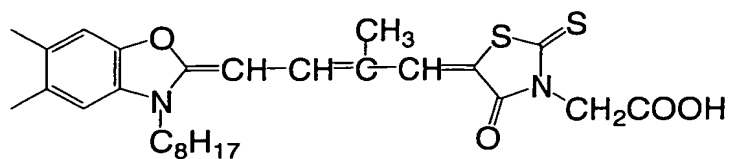
[0291]

Chemical structures of the compounds used in Examples of the invention are shown below.

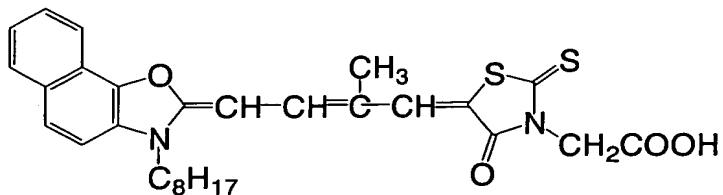
[0292]

[Formula 24]

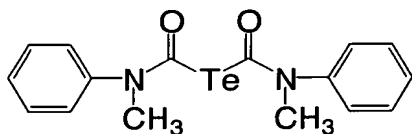
Spectral Sensitizing Dye A



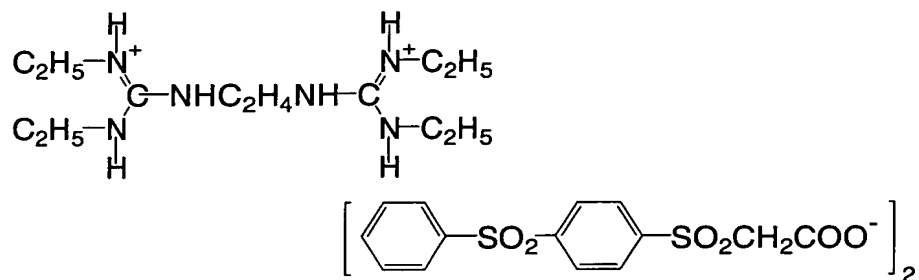
Spectral Sensitizing Dye B



Tellurium Sensitizer C



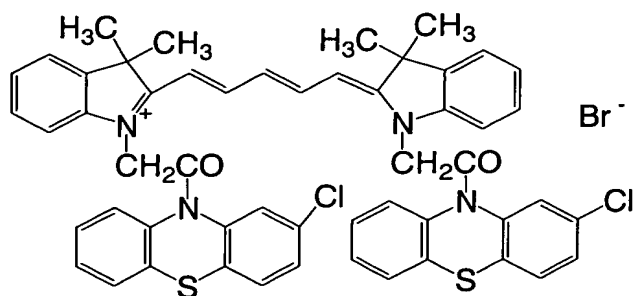
Base Precursor Compound-1



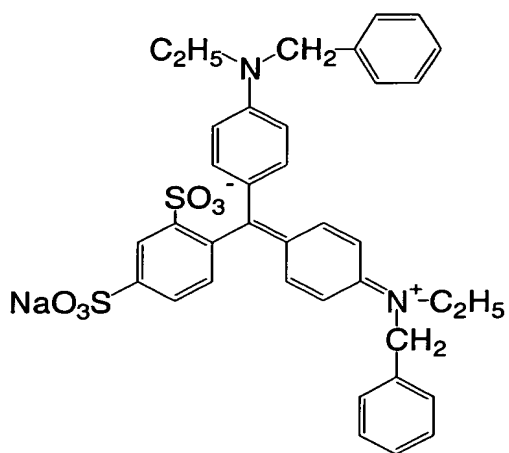
[0293]

[Formula 25]

Cyanine Dye Compound-1



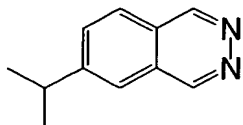
Blue Dye Compound-1



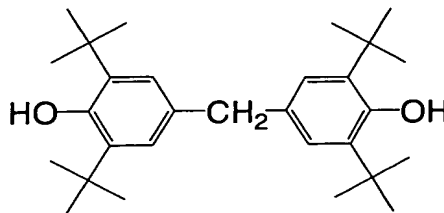
[0294]

[Formula 26]

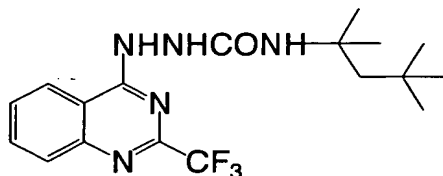
Phthalazine Compound-1



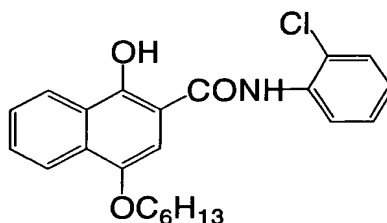
Color-Tone-Adjusting Agent-1



Development Accelerator-1

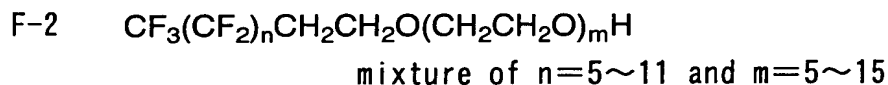
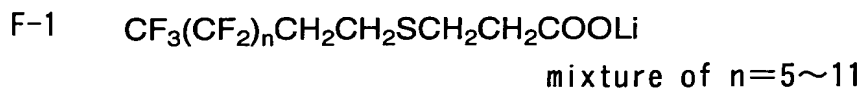


Development Accelerator-2



[0295]

[Formula 27]



[0296]

## 12. Evaluation of Photographic Performances

### 1) Preparation and Packaging Material

Preparation and packaging materials employed were similar to those in Example 1.

[0297]

### 2) Exposure and Development of Photosensitive Materials

Exposure and thermal development (18.8 seconds in total with 4 panel heaters set to be  $105^\circ\text{C} - 105^\circ\text{C} - 121^\circ\text{C} - 121^\circ\text{C}$ ) were performed with Fuji Medical Dry Laser Imager FM-DP L (equipped with 660 nm semiconductor laser having the maximum output of 60 mW (IIIB)). Evaluation of thus resulting images was carried out.

[0298]

### 3) Evaluation of Photographic Performances

Evaluation of photographic performance was carried out in a similar manner to Example 1. The photosensitive materials obtained had a Dma of 4.3 and a  $\gamma$  value of 2.8. Output images of the photosensitive materials had a uniform density. Thus, effects of the invention were observable.

[0299]

### [Effects of the Invention]

According to the invention, there can be provided a method of forming an image using a photothermographic material that provides stable output images with little difference in color tone even in a thermal developing apparatus with high line speed at the time of thermal development.

### [BRIEF DESCRIPTION OF THE DRAWINGS]

[Fig. 1]

Fig.1 is a schematic view of a thermal developing recording device including a laser recording device according to the present invention.

[Fig. 2]

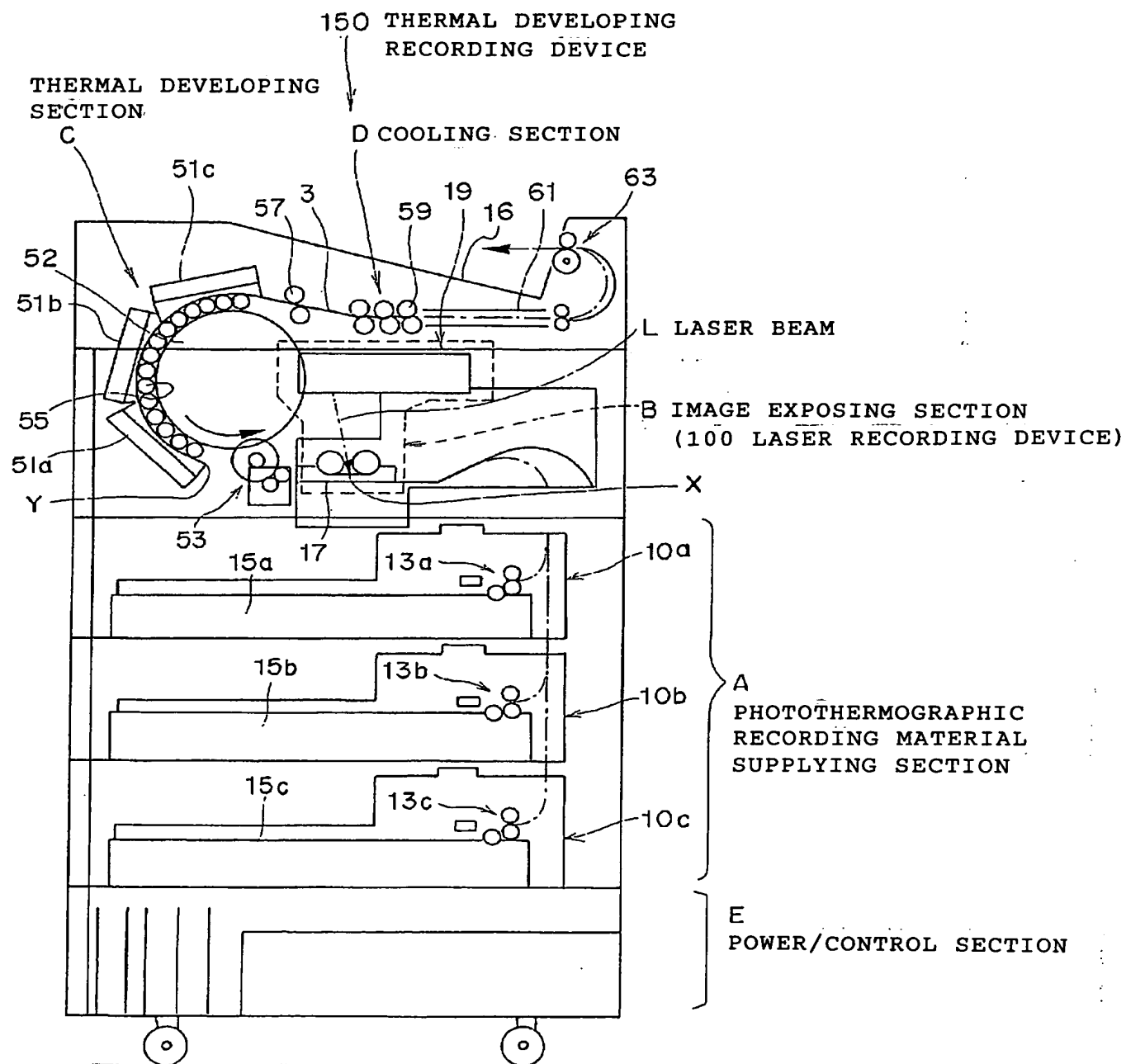
Fig.2 is a schematic view of a conveying section for conveying a sheet of photothermographic material and a scanning-exposing section of the laser recording device.

### [Description of the Reference Numerals]

- 3: photothermographic recording material
- 10a, 10b, 10c: trays for photosensitive materials
- 13a, 13b, 13c: sheet conveyor rollers
- 15a, 15b, 15c: photosensitive materials
- 16: upper light-shielding cover
- 17: conveying section for sub-scanning (sub-scanning means)
- 19: scanning-exposing section (laser irradiation means)
- 21, 22: driving rollers
- 23: guide plate
- 25, 26: sloped portions
- 29: abutting section
- 31: guide plate
- 35: semiconductor laser
- 37: driving circuit
- 39: intensity modulator
- 41: polygon mirror
- 43: converging lens
- 45: mirror
- 51a, 51b, 51c: thermal developing plates
- 52: driving roller
- 53: reduction gear
- 55: opposing roller for conveyance
- 57: cooling rotor
- 59: cooling rotor
- 61: cooling plate
- 63: discharging rollers
- 100: laser recording device
- 150: thermal developing recording device

[DOCUMENT NAME] DRAWINGS

[FIG. 1]





[FIG. 2]

100 LASER RECORDING DEVICE

